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PUBBLICATI NEGLI ULTIMI ANNI IN EUROPA ORIENTALE E PARTICOLARMENTE IN RUSSIA

RAPPORTS SUR LES TRAVAUX DE PHYSIQUE
PUBLIÉS PENDANT CES DERNIÈRES ANNÉES
DANS L'EUROPE ORIENTALE
ET PARTICULIÈRMENT EN RUSSIE

REVIEWS OF WORKS ON PHYSICS
PUBLISHED DURING THE LAST YEARS
IN EASTERN EUROPE
AND PARTICULARLY IN RUSSIA

INTRODUCTION

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President
of the International Union of Pure and Applied Physics

This venture on the part of *Il Nuovo Cimento* had its origin in discussions between the Executive Committee of the International Union of Physics and the Publications Committee of the Union on the need to do something about the inadequate knowledge in many countries of the work on physics published in Eastern Europe and particularly in Russia. This lack of knowledge is due to many causes, of which the most important is the inadequate knowledge which scientists in these countries often have of the Russian language, in which most of this work is written. It was the view of the Executive Committee that the best practicable solution of the problem would be if some scientific journal, with a high international reputation and wide circulation, would each year publish a group of reports about the work in question, describing the research that had been done and its relation to the progress of physics elsewhere.

In April of 1952, during a visit to the Institute of Physics of the University of Milan, I had the privilege, as President of the Union, of discussing the project with Professor POLVANI, President of the Italian Physical Society and Editor of *Il Nuovo Cimento*. Professor POLVANI was at once convinced that the need for such articles existed, and offered the collaboration of *Il Nuovo Cimento* without cost to the Union. The plan was to concentrate all these reports in one *Supplement* to this Journal.

Some months later the Council of the Italian Society of Physics unanimously approved Professor POLVANI's offer and gave him a free hand in this respect, and also the Executive Commitee of the International Union of Physics decided to recommend to the International Council of Scientific Unions that some assistance should be given to the project. They accepted the offer that a *Supplement* of *Il Nuovo Cimento* should be used for the publication of the works in question, and asked Professor G. A. BOUTRY, Secretary of the Publications Committee, and myself to work out the details. Their proposals met with the agreement of the Journal; Professor P. CALDIROLA, Assistant-Director of *Il Nuovo Cimento*, was then asked to accept the scientific editing of the publication. Professor CALDIROLA undertook this by no means light task, and the work has proceeded in an atmosphere of cordial collaboration between the people concerned and many difficulties have been overcome.

Of these difficulties, two are particularly worth describing. The first was the difficulty in finding authors who were able and willing to write the separate reports. This is because there are few Western physicists who know the Slavonic languages, and also because in our libraries the collections of works and periodicals from Russia and from other countries in Eastern Europe are very often incomplete. This has been successfully overcome, and the editors and myself would like to thank all those writers whose works are represented in this volume.

The second difficulty was the proper manner by which the transcription into Latin characters of names and other words written in Slavonic characters should be made. The way this is normally done was found to depend on the language of the author; and, even among writers of the same language, there was often a difference of one author from another and from one period of scientific work to the next. The International Normalising Organization has prepared instructions for this transcription in its Second Draft Recommendation N. 6, dated the 7th January 1953 (*); the editors of the *Supplement* have thought it right to follow their Recommendation in spite of the fact that publications with wide international circulation follow other rules and that to achieve consistency along these rules involves them in considerable work.

Ten reports are published in this *Supplement* and are presented according

(*) See pag. 539 of this issue.

to the alphabetical order of the authors' names, with the exception of the report of Professor TURKEVICH, which gives a brief and general account on the development of the study of physics in Russia, from 1700 to today. It seemed to us reasonable to place this introduction first in the series. The authors come from all over the western hemisphere; the assistance of the Russians was sought, but no answer was received from the Academy of Sciences of the USSR to whom we wrote.

To close this brief introduction, I would like on behalf of the Executive Committee to thank the editors of *Il Nuovo Cimento*, and particularly Professors CALDIROLA and POLVANI, for the arduous and successful work they have undertaken. We would also like to thank all authors for the trouble they have taken with the summaries. In addition, our thanks are due to Dr. R. CORBI of *Il Nuovo Cimento*, who has been in charge of the printing of the *Supplement*; to Prof. G. C. DALLA NOCE and Dr. S. VILLANI, who, with their sound knowledge of Russian, have assisted us to resolve many linguistical problems; and finally to Dr. L. BASILICO, who has been responsible for the checking and final form of the *Supplement* and for the references.

We hope that this *Supplement* will be favourably received and that it will fill a real gap in the knowledge of many scientists in all continents on the progress of physics in Russia and in Eastern European countries. We are sure that the experience gained will be useful for the continuation of this work, and the editors of *Il Nuovo Cimento* are beginning the preparation of a second volume, dealing with work on other subjects of physics published in Russia, and also on some of the most recent work published during the last year.

INDEX OF THE REVIEWS

J. TURKEVICH – Soviet Physics . . . . . pag. 344
R. W. CAHN – Soviet Work on Mechanical Twinning . . . . . » 350
A. L. MACKAY – Recent Soviet Work in the Field of Crystallography . . » 387
A. L. MACKAY – Crystallography in Eastern Europe . . . . . » 415
M. MAGAT – Travaux soviétiques sur la théorie de la liaison chimique . » 416
S. ROSENBLUM – Sur les travaux de magnétisme en U.R.S.S. . . . . » 441
D. SHOENBERG – Recent Research on Superconductivity in the U.S.S.R. . » 459
W. J. SWIATECKI – Polish Physics. . . . . » 481
G. WATAGHIN – Recent Research on Cosmic Radiation in the Soviet Union » 489
J. WILKS – Recent Russian Work on Liquid Helium . . . . . » 509

Soviet Physics.

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(ricevuto il 30 Ottobre 1953)

Soviet physics has its roots deep in Russian history and that of Western science. During his travels in Western Europe, PETER THE GREAT collected a number of physical machines and apparatuses which he housed in a museum in St. Petersburg called the Kunstkamera. When the Imperial Academy of Sciences was founded in 1725 by his successor CATHERINE I the Kunstkamera was associated with it and served as its headquarters. In order to develop science, the Imperial government invited foreign scientists to live and work in St. Petersburg and the roster of the Academy was embellished with names of such renown as LEONARD EULER (1707-1783), DANIEL BERNOULLI (1700-1789) and others. The Western European influence in the Academy was so strong that when a sufficiently large group of native scholars was trained, a reaction developed under the leadership of the great figure of 18th century Russian culture, MIHAEL LOMONOSOV (1711-65). A son of a poor Russian peasant near the Arctic wastes of Northern Russia, LOMONOSOV started in a theological school in Moscow, became a science scholar in the Academy in St. Petersburg and completed his education in Western European universities. On his return from Europe, he worked extensively at the Academy making some interesting formulations of the kinetic theory of gases, the law of conservation of matter and atomic structure. He quarelled constantly with his European colleagues in the Academy. In 1755 he founded the University of Moscow that now bears his name. Russian physicists did not make many momentous contributions to the development of their science in the latter half of the eighteenth and in the nineteenth century. The most prominent physicists were B. S. JACOBI (1801-1874) and I. C. LENZ (1801-1865): their work was well known in the West. However, the work of I. I. POLZUNOV (1728-66) on the steam engine, P. N. JABLOČKOV (1847-94) on the electric arc for illumination, A. N. LODIGIN (1847-1923) on the incandescent lamp

and A. S. POPOV (1859-1905) on the radio was so localized that it did not affect the development of Russian science and technology.

At the start of the twentieth century Russian physics had a sound experimental and theoretical basis for its growth in the work of A. G. STOLETOV (1839-96) on the photolectric effect, B. B. GOLICIN in seismography and P. N. LEBEDEV (1866-1912) on the pressure of light. The excellence of the scientific training given at the two major centers of St. Petersburg and Moscow is attested by the pleiad of highly qualified Russian physicists of the twentienth century. The Revolution of 1917 and the havoc of Civil War that followed had a telling effect on Russian physics. Some of the prominent physicists left Russia and made their contributions to world physics in other lands. Those left behind created the prominent school of Soviet physics.

Science in the Soviet Union is a highly organized cultural activity occupying an important role in Soviet society and directly under the control of the State. Its administrative organs are the USSR Academy of Sciences, the Ministries of Higher Education, Industry, and Armed Forces. The old Imperial Academy of Sciences was transformed soon after the Revolution into the USSR Academy of Sciences and given the key position in the organization, development and control of science in the USSR. The Academy is divided into a number of sections, one of which is the section of physico-mathematical sciences. The President of the Academy is a personage of considerable prominence in the Soviet Union comparable in prestige to a major cabinet minister. Each section of the Academy is administered by a secretary who also serves as a member of the Presidium of the Academy. The section of physico-mathematical sciences has a number of institutes:

a) The Lebedev Physical Institute in Moscow which was directed until three years ago by the former President of the Academy, SERGEI I. VAVILOV. The projects in its program are nuclear science (discovery of the Čerenkov effect), design of accelerators, cosmic ray work, study of the propagation of radio waves, spectral analysis and solid state work.

b) The Institute of Physical Problems was established in Moscow for P. KAPICA when in 1935 he was persuaded to stay in the Soviet Union. It was the center of low temperature physics research. In cooperation with the Armenian Academy of Sciences this institute organized the Erivan Alageth expedition for cosmic ray research by the ALIHANOV brothers. This study was not interrupted during the critical war year of 1943.

c) The Physico-technical Institute in Leningrad was directed by A. F. JOFFE and was concerned with solid state work: dielectrics, semi-conductors, photoeffect, and electron multiplier tubes, strength of materials, atomic physics, cosmic rays and theoretical physics.

d) The Institute of Crystallography continues the Russian crystallographic work of E. S. FEDOROV and JU. V. VULF (1863-1925). Its director A. V. ŠUBNIKOV recently received a Stalin prize for the development of a method for making synthetic rubies.

e) The Institute of Theoretic Geophysics.

f) The Seismographic Institute.

g) The Radium Institute.

h) The Marine Hydrophysical Institute.

The Ukrainian Academy of Sciences has an important institute at Harkov where extensive work is done on low temperature physics. There is close liason between the work of the institutes and the major universities of Leningrad, Moscow, Kiev, Harkov, etc. The government is also insistent that the Academy maintain close liason with industry.

The results of the researches carried out in the Soviet Union are published in the following journals:

a) *Doklady Akademii Nauk SSSR* (= *Reports of the USSR Academy of Sciences*). This journal, which comes out thirty-six times a year in six volumes, contains articles on all branches of science from astronomy to zoology. The articles are no longer than four pages and the material published in the *Doklady* often appears in more extensive form in other journals.

b) *Izvestija Akademii Nauk SSSR, Serija Fizičeskaja* (= *Bulletin of the USSR Academy of Sciences, Physical Series*). It is published by the section of physico-mathematics. It often contains articles presented at physics conferences in the Soviet Union. This journal comes out six times a year.

c) *Žurnal Experimental'noj i Teoretičeskoj Fiziki* (= *Journal of Experimental and Theoretical Physics*). It contains articles full of detail and is of scope and quality comparable to that of the *Physical Review*. It comes out twelve times a year.

d) *Žurnal Tehničeskoj Fiziki* (= *Journal of Technical Physics*). This journal is similar to the *Journal of Applied Physics* and also comes out twelve times a year. Since September 1947 the Soviet scientific journals have discontinued their policy of carrying a title in English or German, in addition to the one in Russian. Furthermore, as of that date, the English or German abstract which usually accompanied the Russian article, was dropped. The publications of two Soviet journals in English, French and German — the *Journal of Physics of the USSR* and the *Acta Physico-Chimica* — were discontinued. This together with the spasmodical receipt of the Russian physics

journals made it increasingly difficult for Western physicists to follow the work of their colleagues in the Soviet Union.

On the other hand Soviet physicists follow the progress of European and American scientists through the receipt of Western journals and through their review journal, *Uspehi Fizičeskih Nauk* (= *Progress of Physical Sciences*). This review journal has both long and short surveys on current development either translated from non-Russian sources or compiled by Russian scientists. The articles are well-written and the topics covered, timely.

Research in physics in the USSR can be grouped around the following topics: cosmic rays, nuclear phenomena, low temperature investigations, solid state physics and theoretical physics. Soviet physicists are also interested in other branches of the subject but the fields mentioned above seem to be coordinated about definite schools of research.

Soviet physicists have been active in cosmic rays for a number of years. D. Skobel'cyn was one of the first physicists to use a Wilson cloud chamber in a magnetic field. There are two main laboratories for cosmic ray research, one in Armenia and the other in Pamir. In the former, the two brothers, A. I. Alihanjan and A. I. Alihanov have attempted to demonstrate the existence of « varitrons » — elementary particles of masses differing from those of the electron, proton and the mesons. Their work has been criticized in the West and also in the Soviet Union by the Pamir school of cosmic rays of Dobrotin, Zacepin and S. N. Vernov. The latter workers have also investigated the East-West effect on cosmic rays and the processes that occur in penetrating showers.

Nuclear physics has also been the scene of Soviet activity. The first cyclotron on the European continent was built in 1937 at the Radium Institute in Leningrad. It is of interest to note that Weksler proposed the basic idea for a proton synchroton independently of E. MacMillan and at about the same time. Soon after the epoch-making work of Hahn and Strassmann on the neutron-induced fission of uranium G. N. Flerov and K. A. Petražak reported the discovery of spontaneous uranium fission. Work in recent years has been carried out on nuclear isomerism, fine structure of alpha-ray lines, the spectrum of electron conversion lines and on nuclear decay schemes.

Low temperature phenomena are studied in two centers in the Soviet Union. The Institute of Physical Problems was organized by P. L. Kapica when he transfered his low temperature work from the Mond Laboratory at Cambridge University to Moscow. It was at this Moscow laboratory that V. P. Peškov discovered the phenomenon of secound sound predicted by L. D. Landau. Since World War II Šal'nikov has carried out a very brilliant investigation of the magnetic field contours on the surface of a lead sphere in the transition temperature range. The other low temperature research center is at Harkov. Disorganized during the War, it has been reconstructed

as is attested by the work of G. LAZAREV on the properties of superconductors under the influence of pressure.

The extensive Soviet work on solid state physics has been directed by A. JOFFE. A pioneer in this important field of modern physics, JOFFE studied under RÖNTGEN in Munich in 1903-06 and has written extensively on the mechanical and electrical properties of crystals. He was for many years the secretary of the physics section of the USSR Academy of Sciences and was the founder and director of the Physico-Technical Institute in Leningrad. The experimental side of the solid state work is characterized by synthesis of materials of unusual electric and magnetic properties and the study of such properties. Thus B. M. VUL was one of the pioneers in investigating the interesting ferro-electric material barium titanate. KUBECKIJ's work on the secondary emission of electrons led to the early development in the Soviet Union of the photomultiplier tube. N. S. AKULOV and V. K. ARKAD'EV have worked on the magnetic properties of matter. The extensive Russian school of luminescence of solids was founded by S. I. VAVILOV, the late President of the USSR Academy of Sciences. The theory of the solid state has been ably treated by such men as I. TAMM, JA. I. FRENKEL, S. I. PEKAR, S. V. VONSOVSKIJ and D. I. BLOČINCEV. TAMM's work on the surface electron states has been recognized by characterizing such states as « Tamm Levels ». The treatises of FRENKEL on wave mechanics, theory of liquids, and electrodynamics are known to all advanced students of physics. His death last year is a loss of a great teacher of physics. S. I. PEKAR, the Professor of theoretical physics at Kiev has worked in semiconductors, while S. V. VONSOVSKIJ and JA. S. ŠUR have published recently a treatise on magnetism. D. I. BLOČINCEV has been extending the Bloch theory of electrons to new limits of applicability.

Soviet theoretical physics has commanded a great respect for a number of years. The name of V. A. FOCK has been associated with quantum mechanical calculations of the structure of the complex atoms. In recent years FOCK has been working on the diffraction of radio waves. L. D. LANDAU is another Soviet physicist whose reputation is solidly established in the world of physics on the basis of his extensive papers on low temperature phenomena and on the theory of solids. Of the many other theoretical physicists particular mention should be made of D. D. IVANENKO (nuclear structure) and I. M. LIFŠIC and ŠAL'NIKOV (low temperature phenomena).

Research in optics has a long tradition in Russia. P. N. LEBEDEV in his measurement of the pressure of light performed one of the notable investigations of classical electromagnetic theory. D. S. ROŽDESTVENSKIJ (1876-1940) studied anomalous dispersion of light and his pupil, S. I. VAVILOV, investigated fluorescence in solution and organized the extensive school of luminescence in the Soviet Union. In his laboratory P. A. ČERENKOV discovered the luminescence effect of fast particles known as the Čerenkov effect, now in-

vestigated all over the world. The Russian investigators in optics, L. T. MANDELSTAM (1879-1945) and G. S. LANDSBERG, discovered light scattering in crystals almost at the same time as RAMAN discovered his famous effect in liquids. It is of interest to note that E. ZAVOJSKIJ discovered in 1945 the paramagnetic resonance of electrons at microwave frequencies.

Soviet physics is active in many other branches of the science as mere perusal of any issue of the *Journal of Experimental and Theoretical Physics* will reveal.

Its contribution to physics has been great, and a larger possibility of scientific interchange with the physicists who live outside the Soviet Union would be desirable for the progress of science.

Soviet Work on Mechanical Twinning.

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(ricevuto il 5 Giugno 1953)

CONTENTS

1. Introduction. – 2. The Shape of a Twin. – 3. The Stages of Formation of a Twin. 1. Introduction. 2. Elastic Twins. 3. Interferometric Study of Elastic Twins. 4. Residual Twins. 5. Stresses for the Various Stages of Twinning. 6. Thermal Hardening of Twins. 7. Influence of the Structure of the Crystal. 8. Experiments with other Substances. 9. Experiments in other Countries. – **4. Effect of Heating on Twin Lamellae.** 1. Reabsorption of Twins by the Parent. 2. Recrystallization and Related Phenomena. 3. Comparison with Work in Other Countries. – **5. Other Observations Connected with Twinning.** – 1. Twinning and Fracture. 2. The Choice of Twinning Elements in Quartz. 3. Pseudo-Twinning. 4. « Thermoelastic » Martensite Compared with Elastic Twins. – **6. Theoretical Treatment of Twin Propagation.** 1. Introduction. 2. The Theory of Lifšic and Obreimov. 3. The theory of Lifšic. – **7. Bibliography.**

1. – Introduction.

Two crystals of the same species, present together in a single coherent piece of solid, are said to be in twin relation to each other if their lattices are related by symmetry about some crystallographically important axis or plane. Such twin pairs may be formed either at the time the crystals grow (from the melt or by transformation in the solid state) or under the influence of applied mechanical forces. We shall be concerned here only with the second variety, often known as *mechanical twins*. They are usually, though not always, generated by a shear process. A particular plane of the parent crystal is selected as *twinning plane* and *each* lattice point on one side of it is translated in the *shear direction* through a distance directly proportional to its distance from

the twinning plane. The shear direction is parallel to the twinning plane. Such twins are often in the form of thin lamellae; in this case the shear is restricted to lattice points within the lamella, which is bounded by two parallel twinning planes. Fig. 1 shows the process diagrammatically, and contrasts it with slip.

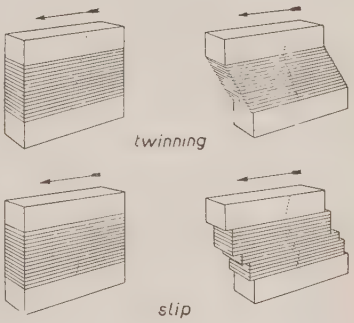

Fig. 1. Twinning and slip (schematic). Each layer represents one lattice plane. The dots define lattice rows.

In metals, twins are commonly lenticular in shape rather than lamellar, unless they pass right across a single crystal. However, such twins are never unless they pass right across a single crystal. However, such twins are nevertheless formed by shear, with respect to the same twinning plane and direction; this is best understood by bearing in mind that the twin forms on both sides of an initial plane lamina, as illustrated in an exaggerated fashion in Fig. 2. The interface between parent and twin (or composition surface) is then not exactly parallel to the twinning plane, but is never far off being parallel. The severe elastic strains in the parent indicated in Fig. 2 give rise to various secondary effects with which we shall be concerned later. (Elastic strains in the twin have been ignored in drawing the Figure).

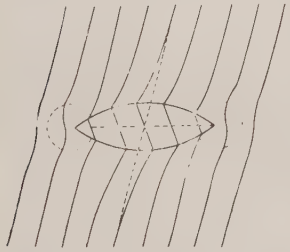

Fig. 2. – Lenticular Twin (exaggerated). Elastic strains in the twin are neglected.

Because the shear is not such that each lattice point is translated to an equivalent position as in slip, and because each individual lattice point is moved and not only some of the points, the twin has an orientation differing from that of the parent crystal. In the case shown in Fig. 1, parent and twins have orientations related by reflection in the twinning plane; this is indicated by the reorientation of the lattice vector included in the Figure. This is the most common relationship, and the Soviet work with which we shall be concerned has been almost entirely restricted to this type of twin.

The questions which have been examined by Soviet scientists comprise: (i) the shapes of twins, (ii) the stages of their formation, (iii) the critical conditions controlling the appearance of these stages, (iv) crystallographic criteria determining the choice of twinning plane and direction, (v) the relation between twinning and fracture, (vi) the effect of heat on twinned crystals and (vii) the theoretical interpretation of the observations. In addition there

have been studies of pseudo-twins which are now recognized as being of a different nature, and a study of twinning in quartz, which differs basically from the process described above. A brief account will also be given of the similarities between twinning and certain aspects of martensitic phase transformations which have been investigated in the Soviet Union.

Twinning was discovered by REUSCH [1] in experiments with calcite, and its widespread manifestations, particularly among minerals, were explored over a long period of years by MÜGGE. This early work was largely of a formal crystallographic character. Subsequently it was studied for some years in the U.S.A. [2]. In recent years twinning has been studied more intensively in the Soviet Union than elsewhere; it would perhaps be correct to describe the Soviet contribution in this field as comparable in importance to the classic work of SCHMID and BOAS [3] in the field of slip. Background information about the state of knowledge about twinning in 1935, which approximately marks the beginning of Soviet work in this field, can be obtained from SCHMID and BOAS' book.

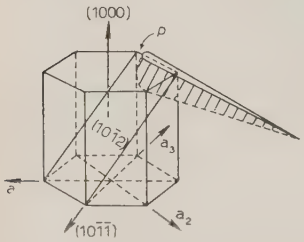

Fig. 3. – Shape of twin lamella in a zinc crystal made by impact at *P*. (10$\bar{1}$2) is the twinning plane, (101$\bar{1}$) is the shear direction. - After JAKUTOVIČ and JAKOVLEVA [4].

2. – The Shape of a Twin.

JAKUTOVIČ and JAKOVLEVA [4] produced twins in cleavage fragments of zinc crystals by pressing or impacting a small sphere on the cleavage surface. A number of thin lamellae radiated from the point of contact. In confirmation of earlier results [5] it was found that impact produced longer rays than static loading. There was no difference in the appearance of the twins if the specimens were cleaved from crystals which had been extended 30% in slip.

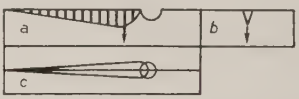

Fig. 4. Twin of Fig. 3 projected (*a*) in the twinning plane, (*b*) in the plane of shear, which includes the shear direction and is normal to the twinning plane, (*c*) along the shear direction. - After JAKUTOVIČ and JAKOVLEVA [4].

The shapes of the twins were studied by sectioning the crystals along various planes. A twin originating within the sample was similarly examined. Figs. 3-5 summarize the conclusions.

The authors emphasized the fact that the twins were always in the form of lamellae, being thin along the direction normal to the twinning plane but spreading readily in this plane. They explained this by remarking that the

residual elastic stresses in the parent crystal on either side of the developing lamella were such as to oppose thickening of the lamella, while in the region defined by extrapolating the existing lamella the elastic strain in the lattice (due to the applied load) was in the same sense as the twinning shear. This can be understood by reference to Fig. 2. The fact that the length of the lamellae (the dimension parallel to the shear direction) increases outside the immediate environs of the impression is attributed to the distortion of the lattice near the impression, which must impede the development of the twin there. Further off, the stress dies away so that the lamellae once again narrow.

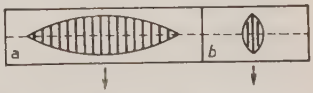

Fig. 5. Twin lamella in interior of a zinc crystal, projected (*a*) in the twinning plane, (*b*) in the shear plane. - After JAKUTOVIČ and JAKOVLEVA [4].

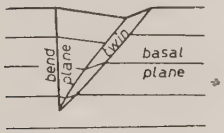

Fig. 6. Accommodation bend associated with a wedge-shaped twin.

Basically this way of accounting for the shape of twins is in agreement with a later quantitative formulation by LIFŠIC (§ 6.3). In one respect the observations of JAKUTOVIČ and JAKOVLEVA contradict the later theory, which predicts that at the leading edge of the twin the interfaces should meet tangentially. It is very probable that this discrepancy can be accounted for in terms of the *accommodation bends* which have been recently discovered in zinc by JILLSON [6], and further studied by PRATT and PUGH [7]. These are planes across which the crystal lattice is slightly titled, and which meet the leading edge of the twin lamella (Fig. 6). These bends are a particular manifestation of a form of slip known as *kinking* (cf. ref. [6]) and their presence is presumably bound up with the high shear stress which must exist near the edge of a twin the interface of which meet at a finite angle, as observed. In the absence of elastic or other accommodation this stress would be infinite at the edge, because A, A' (Fig. 7) are mutually sheared through a distance $s \cdot d$, while B, B' are not displaced at all, a small elastic displacement apart. The strain gradient between A' and B' is thus at any point equal to $s \times$ the slope of the interface at this point, and this changes discontinuously at the edge from a high value to zero. This stress concentration can be high enough to initiate fracture at the twin edge.

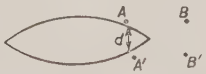

Fig. 7. Displacements near the edge of a lenticular twin.

3. – The Stages of Formation of a Twin.

3·1. *Introduction.*

The experiments to be reported in this section constitute the most original and important Soviet contribution to the subject. Much of the work in question was carried out by GARBER and his collaborators at Harkov, on crystals of calcite, $CaCO_3$, and (Chile) nitre, $NaNO_3$. It should be stated at the outset that, in spite of their interest, the observations made may not be typical for twinning generally, since these crystals are virtually incapable of deformation by slip. For this reason accommodation bends cannot be formed, which in turn limits the shapes which twins can assume. On the other hand, the fact that twinning occurs unaccompanied by any form of slip does simplify the interpretation of the results.

3·2. – *Elastic Twins.*

GARBER cut test specimens out of cleavage rhombs of calcite by means of a wetted thread, in such a way that a twinning plane and direction were normal to one of the surfaces. The surfaces were given an optical polish. When a spherical object or a knife-edge was pressed into the surface, twin lamellae were formed. If the applied load was not too great, the twins disappeared again when the load was removed [8, 9, 10], and they were consequently called *elastic twins* by GARBER. They were always in the form of extremely thin wedges, the maximum thickness being of the order of 1 μ. The length of such a wedge was proportional to the applied load.

Normally, when an elastic twin disappeared on removal of the load, the state of the crystals was indistinguishable from its original condition, but sometimes the elastic twin did not disappear entirely but left behind a small twin wedge, which GARBER called a *stopped elastic twin*. This was rarely observed at room temperature, but more commonly at 400 °C [11]. It appears that the obstacle which prevents the elastic twins from disappearing is either a minute crack held open by a fragment of crystal wedged in it, or (at higher temperatures only) incipient deformation by slip at the point where the load was applied. In either case repeated loading or unloading often removed the obstacle (dislodged the impeding fragment) or else enabled the contracting twin in some other, unspecified, way to overcome it.

GARBER was also able to make ordinary and stopped elastic twins in nitre crystals [12]. The stopped variety were particularly common. He attributes this to the low melting-point of nitre (308 °C as compared with 1289 °C for calcite) implying that nitre was therefore more likely than calcite to be capable of slip, and therefore of localised work-hardening, even at room temperature.

3·3. – *Interferometric Study of Elastic Twins.*

In his earlier work, GARBER used interferometric methods of studying the shape of elastic twins. In one series of experiments, spherical or cylindrical lenses were pressed on the crystal surface and the resulting interference fringes viewed as indicated in Fig. 8. With small loads the fringes merely spread outwards as the lens pressed into the surface, but as the load was further increased, a line discontinuity appeared across the fringes, as shown in Fig. 9. (This figure is taken from the paper by LIFŠIC and OBREIMOV [13], who included it because all of GARBER's figures were poorly reproduced). Further loading produces more discontinuities. On unloading, the elastic twin disappeared again, but it seems that a twin finally disappeared at a stress rather smaller than that at which it first appeared. GARBER did not study this hysteresis in any detail (its existence is inferred from the caption to Fig. 14 in ref. [10]). The peculiar curvature of the fringes in the vicinity of the discontinuity shows that the elastic twin is shaped as shown schematically in Fig. 10. GARBER suggests that at C, owing to some inhomogeneity (dust particle?) there is a local stress concentration, so that the twin starts there. AA' is now the surface trace of the twin lamella (sense of shear as indicated at M), while EA and $E'A'$ are regions of elastic accommodation. The presence of the lens causes the region ED and $CA'D'$ to be further compressed elastically. It is to be noted that the shear component of the force exerted by the lens on the crystal (which depends on the shape of the lens) is of the correct sign only on one half of the area of contact, and correspondingly twins are formed only on this side. GARBER shows that the

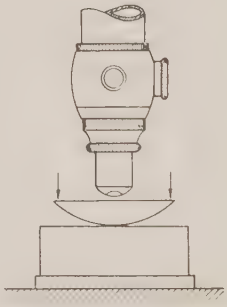

Fig. 8. – Set-up for interferometric investigation of pressure figure. (Crystal is examined by reflected light). GARBER [10].

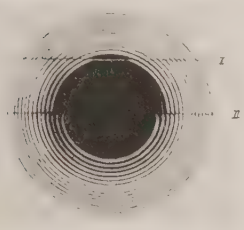

Fig. 9. - Typical interference pattern as seen in the microscope of Fig. 8. - LIFŠIC and OBREIMOV [13].

Fig. 10. – Redistribution of load due to elastic deformation when a twin is formed at point C of contact between lens and crystal. - GARBER [10].

effective shear stress on the twin diminishes rapidly as it grows in thickness, because of the opposing elastic distortions on each side of the twin, and thereafter the twin finds an equilibrium thickness. As the load is increased, so is this thickness.

3·4. – *Residual Twins.*

When an elastic twin, in either substance, had grown large enough, a further small increase of load caused it to spread suddenly across the whole cross-section of the specimen, turning into a thin parallel-sided twin lamella. GARBER called this a *residual twin*: it is the normal type of twin known since Reusch's original experiment. Residual twins, as the name implies, are not affected by removal of the load. Conversion into a residual twin took place when the elastic twin had spread roughly halfway across the section of the specimen. Though experiments were carried out with crystals of different dimensions, unfortunately no figures are quoted which would allow one to find the exact criterion limiting the elastic stage of twinning — whether the elastic twin has to reach a given absolute size, or spread across a given fraction of the cross-section, or approach within a given distance of the far surface. All that it is possible to do is to plot the shear stress at the elastic limit against specimen thickness (i.e. measured along the shear direction) or cross-sectional area. It turns out that there is no correlation at all with the thickness, and only a slight inverse correlation with the cross-sectional area. The stresses at the limit have a fairly great scatter (see § 3·5).

Still further loading caused the parallel twin lamellae to become thicker, while remaining strictly parallel. This was reversible in the sense that a load in the opposite direction would again reduce the thickness of the twin. A continuously increasing load was required to thicken the twin, but at any stage the application of a reversed load of the same value as the instantaneous direct load sufficed to start a reduction in thickness of the twin (see § 3·5).

In ref. [10] GARBER also adds some observations on the genesis of « polysynthetic » twin lamellae (i.e. numerous fine lamellae close together). It seems that this kind of twinning can be produced by loading a crystal cantilever-wise; the loading rod loses contact with a twin lamella as soon as it is formed because it tilts away, and a new lamella is formed nearby where contact has been re-established. Similarly a lens of large radius of curvature produces a dense family of polysynthetic twins.

3·5. – *Stresses for the Various Stages of Twinning.*

Experimental measurements on the stresses for the various stages of twinning are reported in several papers [10, 11, 14, 15, 16]. The four stages,

as listed by GARBER, are as follows:

1) Elastic deformation, without twinning.
2) An elastic twin forms and spreads.
3) The elastic twin changes discontinuously into a residual twin.
4) The residual twin grows thicker.

Stress measurements were mostly made with the specimen held rigidly in a clamp and stressed by means of dead loading, or by a spring. The genesis and behaviour of elastic twins were followed by means of a polarizing microscope, while stage 3 was detected by the sudden drop in load (when spring-stressing was used), and confirmed microscopically.

It appeared that the exact way in which the load was transmitted to the specimen materially affected the ease with which twins could be formed [10]. It was essential to have a concentrated load. When the loading knife or rod was softer than calcite, by Mohs' scratch scale, no twins of any kind were formed even at a stress as high as 600 g/mm², and the specimen eventually fractured some distance from the point of application of the load. This behaviour was attributed to plastic deformation of the knife with a consequent distribution of the load. Harder knives, or a glass rod, produced visible elastic twins under a stress of 20-30 g/mm², *computed over the whole cross-section*. Cracks also appeared at the point of loading. In a later paper [15] it is stated that a piece of paper placed between a hard knife and the crystal surface did not prevent the formation of elastic twins. Indeed it appears that an excessively concentrated load (very sharp knife or point) generally caused cleavage instead of twinning.

In an earlier paper [14] the stress for the appearance of a visible elastic twin was found to be in the range 20-40 g/mm². It is emphasized that these figures are upper limits and that it is probable that smaller twins, too small to see, exist at smaller loads. A graph of twin length against load, given in ref. [11], can be extrapolated to zero length at zero load. Thus GARBER's contention [14], that minute elastic twins appear at the first contact, appears justified. Strictly, this eliminates stage 1 in the above scheme.

The measured stress for the transition of an elastic into a residual twin (again, computed over the whole crystal section) covers a large range of values. In ref. [14] it is concluded that the values fluctuate in the range 150-350 g/mm², while in ref. [10] the figures 150-200 g/mm² are quoted. Individual values for the stress are given only in ref. [14]. As already stated, these values are not correlated with the specimen thickness, and only very weakly with the specimen cross-section (this correlation may well not be significant). GARBER [17], however, states that the limiting stress depends on the specimen dimensions, the nature of the internal stresses present, and the duration of the experiment. No details are given to support these statements; the first

two are probably a periphrasis for saying that there is a spread in experimental values, but the third statement suggests that delayed conversion of elastic into residual twins, at constant stress, was observed.

In ref. [15], measurements are reported of the stress required to make a residual lamella grow thicker. Here a shear stress was applied cantilever-wise some distance from the lamella. The load was applied slowly, and the stress at which the twin had thickened by 1 μ was arbitrarily taken as the limiting stress. It is specifically stated that for a given lamella this stress was the same for reversed loading (tending to reduce the lamellar thickness) as for direct loading. It was possible to make a lamella reverse through all stages, i.e. entirely disappear, by reversal loading. The shear stresses were mostly in the range 90-110 g/mm^2, but in a few cases 40-50 g/mm^2 were recorded. If a crystal had been work-hardened by previous twinning the stress might be as high as 330 g/mm^2.

In another paper [17] in which he discussed the stress-strain relationships in a compressed calcite crystal, GARBER quotes two results obtained by VOIGT [18] in compression tests for the resolved shear stress to create a residual twin. These were 3200 and 7500 g/mm^2! These values exceed those required for twin thickening by a factor of more than 10. GARBER states that the ratio between the two stresses for the same specimen (still in compression) from unspecified experiments of his own, always exceeded 8.

The stress required for thickening a twin lamella is thus considerably smaller than the elastic limit, i.e. the stress needed to make a stable twin. The only reason why the two stages can be separately studied is that the concentrated form of loading used for creating a residual twin does not allow the twin to thicken. In the normal form of tensile experiment with metal crystals, the two stages are telescoped, so that, once a stable twin is formed, it will immediately thicken under a steadily falling load. The load (where applied by a spring) in fact falls until the increased hardening of the twin prohibits further growth. All this happens very rapidly — hence the characteristic twinning cry.

Raising the test temperature of calcite up to 400 °C did not affect the magnitude of the elastic limit [11]. There was no difference from room temperature behaviour except for the greater number of stopped elastic twins. At temperatures approaching that of liquid air elastic twins remained elastic at stress up to 700 g/mm^2. The elastic stage was always terminated by fracture.

3·6. – *Thermal Hardening of Twins.*

A highly interesting series of observations was made by GARBER [15] on the influence of annealing on the value of the stress required for thickening a twin lamella. Residual twins were first made in the specimens and the

stress required to effect a small increase or decrease in thickness measured. The specimens were then heated for various periods and at various temperatures in the range 400-550 °C. This treatment « hardened » the twins in some way, so that a greater load than before was required to make the twins increase *or* decrease in thickness. The ratio of the stresses after and before treatment might exceed 5 (7 hrs. at 510 °C) but was more usually in the range 1-2. The reproducibility, under given conditions, was reasonably good. A new twin created *after* annealing could be induced to thicken at the same stress as the old lamella had required *before* the anneal. Thus two adjacent lamellae in the same specimen might have widely different limiting stresses. From this GARBER argued that the hardening action must be located in the twin/parent interface; he suggests that there may be local cracking, which he considers would lock the interface. This is perhaps not so paradoxical as at first sight it appears, for such cracks might affect the elastic stresses in the vicinity of the boundary in such a way as to oppose further thickening of the twin. However, if this were so, one would expect a reduction of thickness to become correspondingly easier, which is contrary to observation. GARBER's interpretation is therefore suspect.

It is possible that the interface is locked in position by impurity atoms which congregate there. Such locking is known to impede grain growth in certain dilute alloys (e.g. aluminium/manganese). If, as is very likely, twinning involves a dislocation mechanism, then impurity atoms may lock the dislocations. This is known to be the cause of the yield-point in iron/carbon alloys [19]; here also the limiting stress for plastic deformation is raised. GARBER himself points out the similarity. One might expect the limiting stress to decrease again once the interface had begun to move. GARBER does not mention having noticed this, but this may well be due to his having used dead loading. (It is not made clear whether in fact be used it).

GARBER also comments on the resemblance of his results to those of BLANK [20] and KLASSEN-NEKLUDOVA [21], who by annealing deformed rock-salt crystals at 600 °C reduced their flow stress at room temperature from 400 to 100 g/mm², but by annealing at 780 °C raised it again to 200 g/mm². However, according to PRATT [22], this hardening is to be attributed to frozen-in vacant lattice sites.

3·7. – *Influence of the Structure of the Crystal.*

GARBER, ZALIVADNYJ and STARČEV [16] studied the development of twins in artificial crystals of nitre possessing varying degrees of macromosaic — i.e. the crystals were subdivided into small lattice blocks with slight mutual tilts. (This macromosaic, which is a feature of crystals grown from the melt or solution, should not be confused with the submicroscopic structure deduced

from X-ray powder photographs and usually known as « mosaic structure »). The crystals were divided into three groups on the basis of their twinning behaviour:

(i) Those crystals that fractured without forming residual twins. Elastic twins remained small (less than 1 mm linear dimensions).

(ii) Those crystals in which residual twins were formed, but which fractured before the twins could increase in thickness.

(iii) Those crystals in which residual twins became thicker before fracture.

The shear stress in the twinning plane when fracture occurred was in the range 500-1 000 g/mm².

The polarising microscope revealed no differences between these three groups, but X-ray diffraction (Laue) photographs showed systematic differences. In group 1 the relative tilts of the blocks were up to 1°, in group 2 these misorientations were only up to 8′, while in group 3 there were no detectable misorientations (estimated sensitivity 2-3′). It should be added that the Laue photographs reproduced in the paper are so badly printed that no conclusions can be drawn from them. It is unusual for ordinary Laue photographs to be sensitive to misorientations as small as 3′.

3·8. – *Experiments with other Substances.*

Measurements have been made in the Soviet Union of the stresses required for twinning in zinc [24], cadmium [24] and bismuth [25].

Davidenkov, Kolesnikov and Fedorov [23] examined 12 single crystal tension specimens of zinc oriented so that the resolved shear stress on two of the twinning planes greatly exceeded that on the slip plane. Tests were done at various temperatures. The stress needed to create a residual twin, as judged from the associated sudden drop in load, was measured. The chief conclusion which was drawn from these experiments was that this stress was much greater than the critical resolved shear stress for slip (by a factor of 4-10), and that the temperature dependence of the twinning stress was much greater than that of the slip stress. It was also shown that, as a rule, those specimens which had the resolved shear stress also had the highest ratio of resolved stress normal to the twinning plane to resolved shear stress in that plane. From this it is concluded that the value of the normal stress also plays a part in determining the limiting condition for twinning. It should be added that all calculations were done on the unverified assumption that that twinning plane operated on which the resolved shear stress was the highest, (which is inconsistent with the conclusion just mentioned!). The authors themselves remark that too few tests were done for any firm conclusions to be drawn. The shear stresses at which twinning occurred were in the range

400-750 g/mm², according to temperature and orientation. However, a specimen oriented so that no slip occurred at all, on pulling in liquid air had not twinned at a resolved shear stress of 1000 g/mm².

Jakovleva and Jakutovič [24] have measured the relation between the critical resolved shear stresses for twinning and slip, and the diameter of their cylindrical tension specimens, which in this case were single crystals of

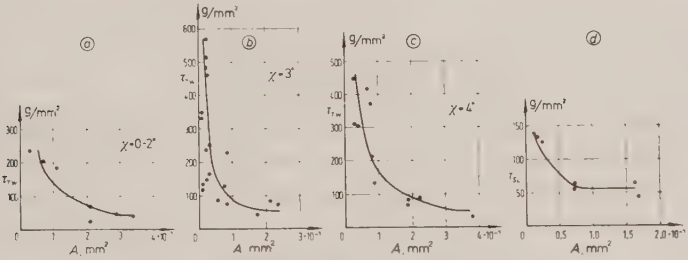

Fig. 11. Resolved critical twinning shear stress τ_{TW} in the twinning plane (*a-c*) or resolved critical slip stress τ_{SL} in the slip plane (*d*), as a function of the cross-sectional area of the cylindrical crystal of cadmium. - After Jakovleva and Jakutovič [24].

« chemically pure » cadmium. These were grown by the Andrade method in wires which had stepwise changes in diameter along their length. This was done with a view to ensuring that the specimens of different diameters had strictly the same orientation and structural perfection. The diameters were in the range 0.09-0.17 mm. The specimens were examined beforehand for uniformity and absence of pre-existing twin lamellae (in view of comments to be made below, it is necessary to remark that only by a painstaking examination at comparatively high power can one be certain that no twins are present). The criterion for twinning was the sound accompanying the sudden growth of a lamella. The estimated errors in the stress values were 10% for the thicker crystals and 35% for the thinner. In Fig. 11 the four published plots are reproduced. The increase of resistance to twinning with decrease of diameter is most striking.

In assessing the significance of these results it is at once clear that this increase of resistance cannot be due to accidental distortion of the thinner crystals during handling, because this would have had the reverse effect of reducing the resistance to twinning (see § 3·9). It does seem, however, that an unsatisfactory way of detecting the onset of twinning was chosen. The volume of a thin twin in a thin crystal is liable to be so small that the accompanying sound may well escape being heard, even in the presence of a resounding foil as used by the authors. The load-drop criterion, when loading is by a stiff spring, is certainly far more sensitive. Any error due to early twins

missed for this reason would be in the right direction to account for, or accentuate, the observed dependence of twinning stress on specimen diameter. The authors do not say how the critical shear stress for slip was defined, but there is less scope for error here.

Gindin and Starčev [25] worked with bismuth crystals made from the melt. The central portion of each crystal was machined to a reduced diameter so that the region where the twin could form should be restricted. Apparently this machining generally left behind a twin lamella in the reduced section. The resolved shear stress at which such a twin began to thicken (under tension) was 140-150 g/mm². Under increasing stress more twins eventually appeared nearby. This happened when the stress resolved in the twinning plane was 215-225 g/mm². Individual values are not given, nor is it stated how many specimens were tested.

In further experiments, twins were created by concentrated loading with a knife along the surface trace of a twinning plane. A sheet of cardboard was interposed between knife and surface, to prevent « severe damage ». If the specimens were thin (less than 1 mm thick) the resulting twins were commonly parallel-sided lamellae going right across the section. In thicker specimens the residual twins were generally wedge-shaped and stopped inside the crystal. (In calcite, presumably owing to the absence of accommodation bending, all residual twins are parallel-sided). It is stated that twinning was obtained much the most readily in specimens having small dimensions measured along the direction of propagation (shear direction?) of the twin. This would appear to be in contradiction with Jakovleva and Jakutovič's findings, but seems reasonable if the diameter effect in bismuth is due to the greater probability, in a thick crystal, of a spreading twin being halted by a structural imperfection of some kind.

A very small load on the knife sufficed to form a twin, and increase of load led to an increase in area of the lamella. This process was completed at an early stage however (sometimes immediately the twin is formed) and thereafter the lamella became thicker as the load was increased further. The spread of the initial lamella, when not instantaneous, occurred in discontinuous stages.

Reversed loading by a knife on the other side of the specimen removed existing twins, but only if they were of the parallel-sided variety. The wedge-shaped twins, therefore, appeared to be locked in position in some way.

3·9. – *Experiments in other Countries.*

It is instructive to summarize for comparison with the foregoing, data obtained by other investigators with cadmium, tin and zinc. Twinning in calcite has not been examined quantitatively elsewhere, while the torsion

technique used in early work with bismuth would render comparison of results here of doubtful value.

MILLER [26] studied twinning in tension in zinc crystals about 10 mm in diameter, and, again, oriented favourably for twinning (DAVIDENKOV *et al.* used crystals 5-7 mm in diameter). MILLER found that the resolved shear stress was the greater, the more nearly the basal plane was parallel to the crystal axes, and he deduced from this that a small amount of slip preceding twinning reduced the resistance to subsequent twinning. The resolved shear stress, at room temperature, was in the range 300-650 g/mm², which agrees well with the values obtained by DAVIDENKOV *et al.* at this temperature (400-600 g/mm²). Both DAVIDENKOV and MILLER used the sudden drop in load as criterion for twinning, and both assumed that twins first formed on the most highly stressed twin plane.

THOMPSON and MILLARD [27] worked with cadmium crystals about 2 mm in diameter. They used a piezoelectric device which was highly sensitive to small sudden changes in load, and therefore to twinning. At room temperature, the resolved shear stress when the first twin appeared was 140 ± 40 g/mm²; at the temperature of liquid oxygen it was 295 ± 45 g/mm². The first of these values is considerably greater than the corresponding value from JAKOVLEVA and JAKUTOVIČ's curves. If these curves are extrapolated to the appropriate cross-sectional area, the twinning stress (by a less sensitive criterion, be it remembered) is seen to be well below 50 g/mm². (In more recent experiments in compression [28], THOMPSON and HINGLEY have on occasion found that much higher stresses did not provoke twinning in cadmium crystals). THOMPSON and MILLARD verified, what most other investigators have merely assumed, that the operative twinning plane was always that one of the 6 possible planes which had the highest resolved shear stress. They also discovered that some twins form after a delay period at constant stress. This « twinning creep » is discussed below (§ 4·4).

KING and his co-workers [28] also made closely similar measurements, on crystals of cadmium of two different grades of purity; the less pure of these was probably comparable with that used by other investigators. The resolved shear stress for twinning with this material was 420 ± 50 g/mm² at room temperature; values for the purer material were approximately in the same range (which compares well with values published by SCHMID and BOAS [3]); by way of contrast, values for the slip stress differed greatly for the two materials. KING confirmed that previous slip affected the twinning stress, but only if this slip had been extensive. In experiments on the size effect, he found that while the slip stress went up steeply with decrease of specimen diameter no clear systematic dependence on diameter emerged for the twinning stress; there were uncertain indications of a reverse correlation!

To complete this picture of disagreement between investigators, we may

quote recent experiments by BELL [28], who has found that zinc crystals oriented so as not to slip, and handled with extreme care, would not twin in tension at room temperature even under resolved shear stresses of 2-2.5 kg/mm². If a reasonably large twin was first produced by accidental bending or by a pinprick, this generally led to further twinning at a stress similar to DAVIDENKOV's and MILLER's values, or slightly higher. We may recall at this point that one of Davidenkov's crystals, which did not slip, had not twinned either at 1 kg/mm².

Taking all observations together, and bearing in mind especially GARBER's insistence on the importance of concentrated loading for starting a twin, it would appear that most investigators have measured the stress required for an already existing twin to grow in extent or thickness. If this is regarded as equivalent to the last stage in Garber's scheme (i.e. thickening of residual twin lamellae) then it can fairly be objected that it should not be a sudden process, and should in any case always proceed under continuously rising load. If, however, we regard the already existing twin as being a *stopped elastic twin*, then the behaviour of metal crystals falls into line with that of calcite and nitre crystals. (Cf. especially the behaviour of twins in bismuth described at the end of 3·8). We may recall GARBER's observation that elastic twins in nitre, which has vestiges of a capacity for slip, are usually stopped, because the lattice near the twin is « hardened » by slip. The behaviour of twins in metals, as just interpreted, is a logical extension of this, for metals can slip easily. The difference in metals is that when the load is removed an elastic twin is stopped almost as soon as it begins to contract. Further stressing will cause it to grow slowly (this is not detectable on the stress-strain record) and then it suddenly spreads across the crystal, becomes residual, and immediately thickens at reduced load.

Under certain conditions there may be a co-operative effect leading to a large « quantum » of twinning and hence to a loud crack and a great fall of load. BELL [28] has shown that this becomes particularly impressive if a pinprick is made in a hitherto flawless zinc crystal while it is already under a high tensile load. This suggests that the K.E. of a spreading twin may be responsible for such behaviour.

The rapid growth of a twin lamella has been elegantly demonstrated in bismuth by FÖRSTER and SCHEIL [29] who recorded « twinning quanta » on an oscilloscope screen through the associated discontinuous changes in electric resistance. The time of formation, depending on orientation, was $0.5\text{-}3.5 \cdot 10^{-5}$ s. When the rapid stage of growth is over, a twin can still continue to grow slowly under increasing load, just as in calcite. JILLSON [6] has confirmed this for zinc, GINDIN and STARČEV for bismuth.

The dependence of the resistance to twinning on the macromosaic structure has not been intentionally examined by anyone besides GARBER and his

co-workers. By way of analogy, the motion of a small-angle intragranular boundary consisting of edge dislocations, which can move under stress, is retarded or stopped altogether when it meets a macromosaic boundary [30].

4. – Effect of Heating on Twin Lamellae.

4·1. – *Reabsorption of Twins by the Parent.*

Garber and his associates carried out many experiments on the influence of annealing twinned specimens on the shape of the twin lamellae. The earliest work [31] was done on calcite and nitre and was followed by studies on bismuth [25] and iron [32]. In these experiments, there was never any recrystallisation in the usual sense (i.e. the appearance of grains of orientations differing from both parent and twin). Papers on recrystallisation are reviewed in the following sub-section.

Crystals of calcite and nitre containing both stopped elastic twins (wedge-shaped) and residual twin lamellae (parallel sided) were annealed for periods ranging from 15 minutes to 20 hours at temperatures up to 900 °C in the case of calcite and up to 306 °C in the case of nitre. The nitre was thus brought much closer to its melting-point (308 °C) than was the calcite (1 289 °C). Correspondingly the effects were more striking in the nitre: all stopped twins were entirely removed at all temperatures bar the lowest, at which some were merely reduced in length. Thin residual twin lamellae progressively disappeared at 306 °C, reabsorption generally starting from several places at once; absorption was the more rapid, the thinner the twin, and thick lamellae were not affected at all. Thin lamellae of the parent crystal sandwiched between two twins assumed the orientation of these twins. The temperatures used were not high enough to affect residual twins in calcite, but the few stopped elastic twins present disappeared or became shortened.

Garber emphasizes that the process of reabsorption is gradual and there is no question of reverse twinning under the influence of thermal or internal elastic stresses. He considers the process to be akin to recrystallisation, with the difference that no third orientation appears.

In bismuth [25] annealing for some hours at 250 °C (melting-point 271 °C) led to the disappearance of thin twin lamellae. Here again only thin lamellae disappeared. Twins 50 μ and more in thickness resisted removal, twins 2 μ and less in thickness disappeared (the critical thickness was not fixed more closely than this). The twins were gradually consumed from either tip, i.e. from the edges of the lens-shaped plates. It is not stated whether parallel-sided twins were capable of being removed; it is possible that they were all too thick.

Garber, Gindin, Konstantinovskij and Starčev [32] studied the removal of twin lamellae (Neumann bands) in pure iron. These twins disappeared on prolonged annealing at 850 °C so long as they did not exceed 1-2 μ in thickness. Twins 8-9 μ thick were not affected even after 150 hours at 900 °C. It was emphasized that absorption always began simultaneously at many places along the twin, dividing its surface trace into an array of short streaks. Each streak then contracted separately. The difference from bismuth was attributed to the fact that twins in iron are parallel-sided as distinct from the lenticular twins in bismuth.

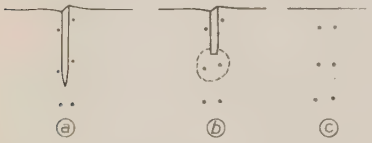

Fig. 12. Progress of the thermally activated absorption of a twin by the parent.

In interpreting these results, Garber has repeatedly emphasized his conviction that the interface between twin and parent in calcite is considerably strained, because twin and parent crystals do not match perfectly; that is, some pairs of atoms are closer together at the interface than they would be in the undisturbed structure. The same has been verified for a twin interface in zinc [33]; it is probably true for all substances that can be twinned. The explanation of the annealing behaviour would then seem to be that if a twin is thin enough, the reduction in surface energy when it disappears more than counterbalances the increase of elastic energy in the surrounding crystal. The observations suggest that absorption proceeds by a thermal activated process akin to grain growth (Garber calls it « recrystallisation ») in which atoms at the edge of the twin lamella move small distances in *random* directions to fit on the elastically strained parent lattice. There is no reverse shear in the strict sense, and restoration of the original specimen shape must proceed in the re-established parent lattice, under the progressive action of the internal elastic stresses, which are particularly great near the twin tip, as indicated schematically in Fig. 12. If reverse shear in the strict sense did occur the twin would be removed by a gradual decrease in thickness, and would at all stages taper to a point, which is contrary to observation.

4·2. *Recrystallisation and Related Phenomena.*

A number of studies [34-37] have been made on the behaviour on annealing of twins in zinc monocrystals. It was firmly established that slip alone, whether or not the crystal was also bent, did not suffice to provoke recrystallisation [34]. If the crystals contained twins, however, nuclei were formed at the interface between twin and parent and these usually grew out into the parent [34-36]. The new grains had orientations differing from both parent and twin. Nuclei became active particularly quickly where twins on different systems met, but

isolated twins could also give rise to nuclei [35]; the time for a nucleus to grow to visible size was the shorter, the thicker the twin at the boundary of which the nucleus was formed [35]. The new grains never grew very far away from the twin which had given them birth — i.e. the untwinned crystal not only could not nucleate new grains but could not even support their growth.

Zolotov [37] investigated the orientations of the new grains growing out ot twins and concluded that their hexad axes usually deviated by less than 10° from the hexad axis of the twin. Such a sharp texture was not found in all specimens, but there was always a « sufficiently distinct preferred orientation ». While this last statement can be accepted with confidence, the analysis of the positions of hexad axes is suspect. This was based on orientation determinations under a microscope, using reflections from etch pits obtained by attack with hydrochloric acid; Zolotov says that the pits are parallel to the basal plane, but in fact facets of many other planes are generally exposed too. These experiments, which are of considerable interest for nucleation theory, deserve to be repeated by X-ray diffraction methods.

There has been some argument among the Soviet scientists as to whether the interface region, the twin itself, or the part of the parent lattice bordering the twin has the highest free energy. All the results quoted fit the hypothesis that the interface is the least stable. If Zolotov's orientation determination is correct, then the side of the interface region nearer the twin should be the most distorted, if one assumes, as he does, that small strain-free regions immediately in contact with highly distorted lattice act as nuclei. This view is in consonance with current views on recrystallisation nuclei.

Some other observations reinforce the conclusion that the twin boundary is highly strained. An etching reagent tends to attack the boundary particularly fiercely [37]. Annealing a twinned zinc crystal in vacuo caused preferential evaporation at the twin boundaries (Bol'šanina and Pavlov [38]). In the same paper it was shown that the activation energy for the diffusion of mercury into a zinc crystal was much reduced if twin boundaries were present; deformation by slip had no such effect. (This conclusion is based on a single twinned specimen, and the experimental technique is so scantily described that it is difficult to form an estimate of the reliability of the conclusion).

4·3. – *Comparison with Work in Other Countries.*

Numerous observations on the annealing characteristics of twins have been published, some of them mutually contradictory. Miller [26] reported that new grains which appear on annealing along twin lamellae in zinc have farily uniform orientations. These were not determined, but qualitatively this observation supports Zolotov's contentions. Jillson [6] confirmed that nuclei

appeared preferentially at the meeting-points of twins, and also that thin lamellae (but not thick ones) were often reabsorbed by the parent. This was not observed by the Russians, and is in fact in conflict with their remark that thin lamellae sometimes grew at the expense of the parent. Both phenomena have been reported for zinc by MATHEWSON and PHILLIPS [39], and for iron [40, 41]. KRIVOBOK's [40] experiments made it quite clear that the swelling of twin lamellae occurs without any change of orientation, for when neighbouring lamellae had swollen enough to become joined, the join was not attacked by etchants, showing that there was no orientation difference there. In uranium, also, both absorption and swelling, as well as preferential evaporation, at a twin have been observed [42]. Absorption took place from the edges, as in the case of bismuth; swelling could go to extremes and produce large new grains. As in the experiments of the GARBER school, all these processes always started at the edges of twin plates and then worked inwards or outwards. The twin interface itself, which is approximately parallel to the twinning plane, did not move.

The experiments of BOL'ŠANINA and PAVLOV [38] on the diffusion of mercury into zinc are contradicted by results obtained by FENSHAM [43], who found that the rate of self-diffusion of tin was no faster at twin interfaces than inside a grain. Self-diffusion at an ordinary grain boundary was faster, but not if the orientation difference across it was small; since this kind of boundary is known to be of low energy, FENSHAM concluded that the same was true of a twin boundary in tin. This observation is consistent with the reported inability of mechanical twins in tin to give rise to recrystallisation nuclei.

5. – Other Observations Connected with Twinning.

5·1. – *Twinning and Fracture.*

In common with those in other countries, Soviet investigators have supposed there to be a close connection between fracture and twinning, and this has given a contributory impulse to twinning research. DAVIDENKOV [44] in particular has been quoted as holding this opinion. Although recent research (e.g. LOW and FEUSTEL [45]) has gradually built up a body of evidence against any direct connection between these processes for the case of steel, to which the most interest attaches, at least one interesting paper has appeared in which a connection has been shown to exist (JAKOVLEVA and JAKUTOVIČ [46]). Zinc crystals were compressed in a direction almost normal to the basal planes. This led to twinning only, since the resolved shear stress along the basal (slip) plane was slight. Kinking, too, depends on the existence of a component of applied stress parallel to the basal plane. The crystals thus had no means

of relieving the stress concentration at the edges of the lamellae, and the result was local cleavage along a prism plane of the first order, $\{10\bar{1}0\}$. Where such a crack abutted on a neighbouring twin lamella, it traversed this by cleavage along a basal plane in the twin. This plane is inclined at a small angle to the prism plane in the parent, so that a sectional view of the complete crack assumes the shape of a squat parallelogram. The neighbouring twin in turn terminated at another crack, and in this way a staircase of twins and cracks was propagated through the crystal (Fig. 13). In the direction normal to the plane of the sketch, the cracks and twins went right through the crystal. The shape of the twins was thus consistent with the authors' earlier observation [4] that twins are comparatively narrow measured along the shear direction. If such a specimen was further compressed, it broke entirely; no doubt the fracture spread from the already existing cracks along the twin interfaces.

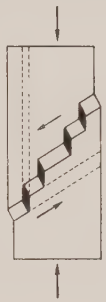

Fig. 13. – Staircase pattern of twins (outlined) and cracks (black) in a zinc crystal compressed along the hexad axis. - Jakovleva and Jakutovič [46].

This behaviour was limited to tests at the temperature of liquid air. At room temperature sufficient capacity for slip apparently remained, even under the small resolved shear stress in the basal plane, for twinning to proceed without fracture. The specimens tested in liquid air changed significantly in density (by up to 0.75 %), while those tested at room temperature did not. This showed that the configuration of Fig. 13 actually formed inside the specimen and not just as a consequence of sectioning.

These observations are closely analogous to those by Rose [47], who examined calcite. Here even the thinnest parallel-sided twin, if it terminated inside the crystal, caused local fracture in the parent, sometimes in a stepwise fashion. In Jakovleva and Jakutovič's paper there is a remark which suggests that the twins had to be rather thick before any cracks were visible. These experiments clearly demonstrate that the thick lenticular twins we find in metals owe their existence to the capacity of metals to deform by slip and kinking.

Distinct from the above type of fracture is the so-called *parting* of a twin lamella from the parent along one of the interfaces. Such parting can be very perfect, especially in calcite [48] (which verifies the parallelism, on an atomic scale, of residual twins in calcite). Soviet workers have little to say about this phenomenon. The only relevant comment is by Davidenkov *et al.* [23], who state that their tension specimens often fractured along thick twins.

The occurrence of parting is contributory evidence that there is a condition of intense local strain at the interface.

5·2. – *The Choice of Twinning Elements – Twinning in Quartz.*

The two topics of the title are here considered together because STEPANOV [49, 50] has sought to link them together.

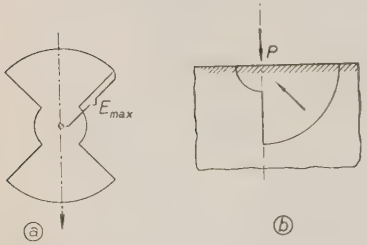

Fig. 14. – (*a*) Section of Young's modulus figure for an idealized crystal. The arrow represents a symmetry axis. (*b*) Section of idealized crystal bounded by a plane, with Young's modulus figure included in appropriate orientation. A load is applied at *P*. - STEPANOV [49].

STEPANOV first set himself the problem of finding a criterion that would decide which plane and direction in a crystal should function as twinning plane and shear direction. He makes the hypothesis that the choice depends on the elastic properties of the crystal, being led to this conclusion by the thought that since twinning is a universal property of crystals (which is, incidentally, far from being correct) some property common to all crystals must be sought as determining factor. He considers the following idealised, twodimensional case: Let a crystal have a Young's modulus E depending on direction as shown in Fig. 14*a*, in which the radial vector from origin to curve gives the values of the modulus for any direction. Let a semi-infinite plate be cut out of such a crystal in such a way that a direction in which a discontinuity in the Young's modulus occurs is normal to the surface (14*b*), and let a concentrated force be applied as shown. Then this load will be taken up unevenly by the plate because it is stiffer in some directions than in others, and this in turn affects the distribution of stress in a given direction at different points in the plate; parts of the plate which are in a « stiff direction » with respect to the point of loading will take up a disproportionately large part of the load. Fig. 15 shows how the normal stress σ_x and the shear stress τ_{xy} are distributed at unit distance from the point of loading. The load is taken up chiefly by the right hand side.

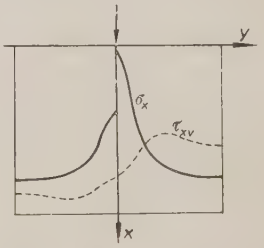

Fig. 15. – Stresses σ_x and τ_{xy} at different points unit distance from the point of loading, for idealised crystal. - After STEPANOV [49].

STEPANOV considers that the free energy of this configuration is larger than

it would be if the same load were applied to a specimen which is elastically isotropic and had $E = E_{max}$ (cf. Fig. 14*a*). The strains and therefore the elastic energy would be smaller. Just such a specimen can be created, in the idealised case being considered, if the left hand side of the plate of Fig. 14*b* is twinnde with respect to a twinning plane normal to the free surface. This twinning plane then acts as a mirror relating the orientation of the two halves and the result would be as shown in Fig. 16. In practice, of course, only a limited amount of material would twin (a lamellar twin) but this does not affect the conclusion that the elastic energy is thereby reduced The shear direction is taken to be parallel to the applied force. (It is not clear why this is specified; since the treatment only takes into account the lattice orientations before and after twinning and not the macroscopic distortion accompanying the twinning shear, the direction of this shear would seem to be beside the point).

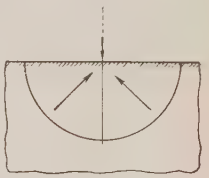

Fig. 16. – Section of idealised crystal, with Young's modulus figure, after twinning. The long arrows represent the symmetry axes in parent and twin. - STEPANOV [49].

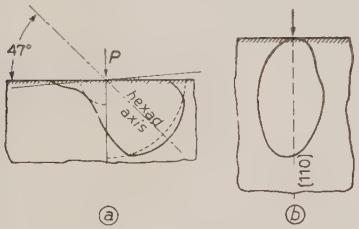

Fig. 17. – (*a*) Section of zinc crystal in plane of shear, with Young's modulus figure. (*b*) The same for calcite. - STEPANOV [49].

STEPANOV's criterion may be expressed in the form: that plane will act as twinning plane which divides the Young's modulus surface into two parts as dissimilar as possible. This criterion has been tested by STEPANOV for zinc, iron, bismuth, antimony, cadmium, magnesium and calcite. The analysis works quite nicely for zinc (Fig. 17*a*). For the other substances the dissimilarity between left hand and right hand sides of the Young's modulus surface is less marked, and in one or two cases there is virtually no anisotropy (Fig. 17*b* for calcite). The author concludes with a reminder of the speculative character of his theory.

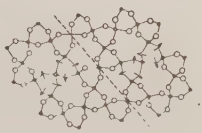

Fig. 18. – Atom positions for a Dauphiné twin in quartz, projection in (0001). Filled circles represent Si atoms. Some oxygen sites are indicated by open circles, others by arrows representing dipole moments. The interface (broken line) is parallel to the diad in either half. - MEGAW [51].

In his second paper [50] STEPANOV applies this theory to the twinning of quartz. Quartz can be twinned in several different ways during crystal growth,

but only one of the types of twin will respond to mechanical stressing. These are *Dauphiné* twins, the orientation of which is related to that of the parent by a rotation of 180° about the three-fold symmetry axis. Fig. 18 (due to MEGAW [51]) shows the change of structure across a boundary between parent and twin. There is no mirror relation with respect to the interface, which can indeed assume any position. In the figure it is shown parallel to a diad axis. Twinning does not involve a shear, for this would cause intolerable strains in the firmly bound homopolar structure; the parent is converted into the twin through a small movement by each oxygen atom (open circles) away from one silicon atom (filled circles) and towards another. Each oxygen atom undergoes its small motion as the boundary sweeps past it, but the movements do *not* result in any macroscopic change of shape. (*) This mode of twinning thus differs fundamentally from ordinary shear twinning.

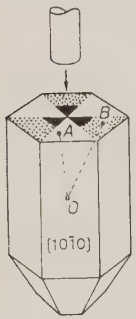

Fig. 19. – Diagram to illustrate Stepanov's theory of impact in quartz. The black sectors are twinned.

CINSERLING and ŠUBNIKOV [52-54] were able to produce and move twin interfaces of this kind by concentrated impact loading of quartz crystals; each impact figure was surrounded by a pattern of twins, of a shape depending on the indices of the crystal face. STEPANOV claims that this can be understood on the basis of his theory, (though there is here no question of shear).

Fig. 19 represents the reviewer's attempt to interpret Stepanov's treatment diagrammatically. A rod is made to strike a (0001) face of a quartz crystal. Let O be a point, inside the crystal, which lies on a line parallel to the threefold axis and passing through the centre of the impact figure. Then STEPANOV states (it is not clear whether this is postulated or has been checked) that for points such as A, lying in any of the unshaded sectors of the (0001) face, corresponding directions OA are associated with a high Young's modulus, while directions such as OB, where B lies in the shaded sectors, are directions of low stiffness. If twins form in the shaded sectors, the lattice in them is reoriented in a way formally described by a 180° rotation about the threefold axis, and this would bring B into an unshaded sector — i.e. the lattice in the twins would become stiffer, as required by STEPANOV's criterion.

CINSERLING and ŠUBNIKOV found just such a sectorial pattern of twins, but it is not clear from STEPANOV's paper which of the two sets of sectors in fact became twinned, the « stiff » or the « less stiff » ones. (The *observed* twin sectors are related to the (1010) face as shown in Fig. 19). This question is of importance, as we shall show in the next paragraph.

(*) The change in stiffness due to twinning does cause a minute elastic strain.

THOMAS and WOOSTER [55] have recently published a study of the stress-induced motion of existing Dauphiné twins in quartz at elevated temperatures (they call this phenomenon *piezocrescence*), and found that the configurations they obtained under a variety of controlled stress systems (flexure, torque) could be accurately interpreted on the hypothesis that « the whole crystal yielded as much as possible under a given stress, i.e. stored up the *maximum* elastic energy » (reviewer's italics). They were originally led to this idea by the observation that applied torque about a particular axis would cause the boundary to move in a given direction for *either* sense of the torque. Their conclusion is in flat contradiction with STEPANOV's ideas, but, as we implied in the preceding paragraph, it does not necessarily contradict CINSERLING and ŠUBNIKOV's observations.

As THOMAS and WOOSTER point out, their hypothesis is simply an application of le Chatelier's Principle, for the crystal is modified so as to accommodate the constraint. In the Soviet paper, on the other hand, it is postulated that the crystal will seek to resist the constraint, which is thermodynamically unsound. In other terms, the lowest free energy here requires the maximum elastic energy. STEPANOV's criterion can still be applied if it is exactly reversed; fortunately this will not alter the predicted twinning plane.

To complete this section, reference should be made to an article by PÉREZ [56] who also examined twinning and untwinning in quartz under the influence of stress and raised temperature. He cites evidence to show that the surface energy of the Dauphiné twins will also affect the precise configuration stable under a given stress system, and also shows that when the boundary moves at all, it does so very rapidly, suggesting that some activation barrier has to be overcome.

5·3. – *Pseudo-Twinning.*

We shall discuss here some crystal processes which have been fallaciously interpreted as twinning.

When rocksalt crystals are compressed, strips of the surface become tilted through a small angle, which varies from strip to strip (BRILLIANTOV and OBREIMOV [57, 58]), and may not be quite uniform across the width of a strip. The lattice planes originally parallel to the surface remain parallel to the surface after tilting [58]. (OBREIMOV, in these and later papers, has called these tilted regions *twins*). This behaviour is exactly what would be expected if the crystal had become kinked. Dislocations, of just the kind that operate in normal slip, collect in planes approximately normal to the slip direction, so that the lattice becomes sharply tilted at these planes, as observed. The observed « twinning plane » is almost normal to the slip direction. The angle of tilt depends on the concentration of dislocation in the boundaries; it is

indeed a characteristic of this type of deformation that the tilt of a *kink band* can be progressively increased by continuous stressing [59]. PRATT [60] in exhaustive experiments on the mode of plastic deformation of rocksalt has shown that the tilted regions are indeed a product of kinking and bear no relation to twinning. The fact that the blue colouration induced in rocksalt by X-rays, which is an index of the state of strain, is concentrated in the boundaries of the «twins» [57], is consistent with the kinking model, because the boundaries are full of dislocations.

In their second paper [57] BRILLIANTOV and OBREIMOV say that evidence of slip in rocksalt should be provided by those who doubted that their bands were twins. This was done by TERMINASSOV [61], and more recently by PRATT [60], by a polarised light technique. In any case, the capacity of rocksalt for slip follows from the fact that rocksalt crystals can be *stretched* plastically without any surface tilts appearing. BRILLIANTOV and STARČEV [62] and STARČEV [63] have, however, continued to regard their observations as instances of a special kind of twinning. The most recent rearguard shot was fired by OBREIMOV in his paper with LIFŠIC [13].

Since some confusion appears to exist as to the phenomena covered by the term *mechanical twinning*, the following will serve as a definition which will probably be acceptable to most crystallographers: The orientation of a twin and its parent are related either by reflection in a rational lattice plane or by rotation (through a simple submultiple of 360°) about a rational lattice direction. The process whereby the lattice changes to its new orientation is either shear, or the motion of an interface unaccompanied by appreciable change of shape. *In neither case is the orientation relationship continuously variable.* For this reason the phenomenon in rocksalt cannot be called twinning. BRILLIANTOV and OBREIMOV [57] gave as another reason for calling their bands by the name of twins, that the transformation took place gradually, as in the thickening of a calcite twin. But in fact kink bands, including those in rocksalt, are tilted simultaneously throughout their volume, the angle increasing gradually with strain; this differs from the addition of new layers in a fixed new orientation, as in true twinning.

GARBER [64] has recently made some novel observations in this field which are formally similar to certain observations on the twinning of calcite; however, GARBER refers to the deformation of rocksalt as *translation* (i.e. slip). He deformed rocksalt crystals in pure shear and examined them meanwhile between crossed Nicols. Internal slip bands were clearly visible owing to their associated birefringence, while interferometric examination of the surface revealed narrow tilted bands. By reversed stressing GARBER succeeded in removing both the slip band and the tilted surface bands. This was possible even when the crystal had first been caused to undergo double slip in compression; the reversed stressing in shear then removed only one set of slip

bands. GARBER also states that he observed *elastic slip*, i.e. birefringent slip bands appeared on stressing and disappeared again when the stress was taken off.

Another instance of kinking being mistaken for twinning is the report [65] that bismuth can twin on the {751} plane, with variable tilt. Expressed in Miller-Bravais indice this plane is $\{22\bar{4}1\}$, which is very nearly normal to the slip direction $\langle 11\bar{2}0\rangle$, as would be expected for a kink band.

In one of his papers, OBREIMOV quotes an observation by ELAM [66] as confirmation for his interpretation of his results for rocksalt. ELAM found that certain aluminium crystals became divided into clearly demarcated regions of different orientations and surface tilts. She called these regions twins. The experiments were repeated by RYBALKO and JAKUTOVIČ [67], who found that the behaviour quoted was restricted to crystals the tensile axes of which were parallel to a cube plane (stereographically, the axes came on the [100] - [110] edge of the unit triangle). Such a crystal is unstable with respect to choice of slip plane, for while the resolved shear stresses on two slip planes are exactly equal to begin with, the lattice rotation associated with the operation of either *one* plane causes the resolved stress on that plane to rise progressively. As a consequence, no doubt, of minor irregularities of structure or orientation, the crystal splits up at the start into regions which slip one or other of the alternative systems. This division is necessarily maintained as deformation proceeds and each region tilts about a different axis. In spite of repeated claims to the contrary, no convincing evidence for the existence of mechanical twinning in face-centred cubic metals has ever been produced.

5·4. – « *Thermoelastic* » *Martensite Compared with Elastic Twins.*

There is a class of diffusionless phase transformations which take place by a shearing process very similar to, though not identical with that of twinning. These are *martensitic transformations*. Until recently it was thought that such transformations always took place by virtually instantaneous shears of portions of the metastable phase to form individual martensite plates. This is very similar to the sudden conversion of an elastic twin into a residual one. Indeed, oscillographic studies have shown that martensite plates in a carbon steel, and twin lamellae in bismuth, form at much the same rates (within 10^{-4} s) [29]. Once formed, a martensite plate normally does not grow further. Recently, however, at least two alloys have been found in which martensitic plates formed at a comparatively high temperature grow in stages as the temperature is lowered in stages. If the temperature is raised again, the plates contract, and there is little temperature hysteresis. This is closely analogous to the behaviour of an elastic twin and, less closely, to the slow growth of a residual twin.

The alloys referred to are an aluminium bronze of approximate composition Cu, 14.5 % Al, 1.5 % Ni [68], and an alloy of composition Au Cd [69]. The phenomenon, which has been called *thermoelastic equilibrium* by KURDJUMOV, has also been explained by him [68, 70]). The change in free energy G due to the formation of a martensite plate is given by $G = -V \cdot \Delta\Phi + E_s + E_e$, where $-\Delta\Phi$ is the decreases in specific free energy of the system due to the greater thermodynamic stability of the martensite, V is the volume of the plate, and E_s and E_e are opposing terms giving the surface and elastic energies associated with the plate. E_e rises steeply as the plate grows, and therefore G passes through a minimum for a particular size of plate. If this size is insufficient for the continuity between the lattices of the two phases to be broken, then the plate exists in thermoelastic equilibrium. If the temperature is changed the value of $\Delta\Phi$ will change too, and the plate grows or contracts till a new equilibrium is found. It seems to the present writer that the most important condition for such an equilibrium to exist is that the specific volume change associated with the transformation should be small, or else the lattice continuity will be broken before the plate reaches its equilibrium size. Indeed for the Au Cd alloy the volume change is only 0.35%, as compared with 2.8-2.9% for carbon steel, which does not behave thermoelastically. No figures are available for the aluminium bronze.

KURDJUMOV points out the relationship between this phenomenon and elastic twinning, with the place of elastic stress being taken by temperature. Although it has not been reported, one would expect the martensite plate, when large enough, to lose continuity with the parent and so to become stable (in the sense that a considerable rise of temperature would be needed before the plate began to disappear). This would be precisely analogous with the formation and removal of a residual twin and its associated stress hysteresis. KURDJUMOV considers that loss of continuity is the factor limiting the growth of individual plates in martensitic transformations generally.

Elastic stresses themselves sometimes affect the formation of martensite plates, as would be expected on le Chatelier's Principle since the martensitic shear causes a change in shape. REYNOLDS and BEVER [71] have found that a stress applied to metastable 60/40 β-brass caused a number of martensitic plates to form. Removal of the stress led to the disappearance of some of the plates, though a faint residual mark remained. On reapplying the stress, plates formed again in the same places. Slow increase of the stress caused slow growth of some plates. It would seem that these observations can be accounted for on Kurdjumov's theory since an external stress will reduce the term E_e for suitably oriented plates, and therefore the equilibrium size of plates at a given temperature would alter. This behaviour is even more closely analogous to that of elastic twins.

Yet another phenomenon in this field has its twinning analogue. KURD-

JUMOV and MAKSIMOVA [72, 73] and MAČLIN and COHEN [74], among others, have found that under certain restricted circumstances martensitic transformations can occur progressively while the sample is held at constant temperature. Applied stress in many cases promotes such isothermal transformation. Analogously, THOMPSON and MILLARD [27] found that if cadmium crystals, which already contained some twins, were held under a constant stress, twinning went on in bursts over a period of some minutes at a decreasing rate. This happened at room temperature, but not at the temperature of liquid air. It would appear that thermal fluctuations play a part in both processes.

6. – Theoretical Treatment of Twin Propagation.

6·1. – *Introduction.*

The first attempt at a theoretical treatment of the propagation of a twin through a crystal was made in the classic paper of FRENKEL and KONTOROVA [75]. Their fundamental contribution was the extension of the concept of wave-like propagation of strain (i.e. the propagation of dislocations) from slip to twinning. In their view, « the mechanism of both twinning and slip is the same; slip differs from twinning only in that the atoms are transferred not to symmetrical, but to equivalent equilibrium positions ». On their model, some atoms are always in positions intermediate between those they would occupy in the parent and those they would occupy in the twin; such a group of atoms is what is meant by the term *dislocation*.

It is difficult to say definitely whether the newer treatment by LIFŠIC and OBREIMOV [13] can be called a dislocation theory. Some such theory seems inescapable when one bears in mind that the applied stress empirically required to make a twin grow will produce an elastic shear strain only about 0.001 of the twinning shear. Thus at such stresses it is impossible to form a whole twin layer at once. The co-operation of the group of atoms constituting a dislocation allows a twin layer to be formed progressively at much smaller stresses.

The above-mentioned theory does not apply to the problem of thickening of a residual twin but only to the growth of an elastic twin. For a residual twin, the main problem is the purely geometrical one of finding a dislocation which will climb through a lattice layer as it propagates across that layer, so that *each* individual layer shall be sheared through the right distance, and will also satisfy certain other geometrical conditions. This is in general a tricky problem, though it has been solved for iron [77] and attempts have been made for cadmium [27]. The main difficulty is that in any such theory

it proves essential to postulate that small twin nuclei are present from the beginning (Thompson and Millard [27], Bilby [28]), and the theories themselves say nothing about how such a nucleus comes to be formed. It would seem that this difficulty can in principle be overcome by Lifšic and Obreimov's theory. A basic assumption of the theory is that very large elastic strains, comparable with the twinning shear, can exist near the point of application of the load, without causing fracture. This allows a group of atoms just under the loading point to be sheared through large distances, and so to snap over to the twinned position one by one. In effect, a dislocation is *created* by the concentrated stress. This twin dislocation is then propagated as the load is raised. Initially the twin is a monolayer, while later on new layers are nucleated under the loading point. In this formulation Lifšic and Obreimov's paper is seen to involve dislocation concepts, but this nowhere comes out explicitly, and the peculiar geometrical properties of dislocations (e.g. the fact that they form closed loops in a crystal) are not considered.

6·2. *The Theory of Lifšic and Obreimov.*

Lifšic and Obreimov [13] have constructed an atomic theory of twin propagation, i.e. one which takes account of the discrete atomic structure of the crystal. An idealized model of a monoclinic primitive lattice with atoms at the lattice points is used. (Fig. 20). The primary purpose of the theory is to interpret Garber's results with calcite.

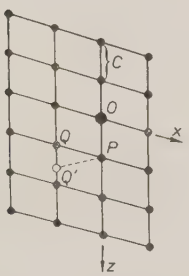

Fig. 20. – Primitive Lattice. with atoms at lattice points. A load parallel to the z-axis is applied at the origin O. - After Lifšic and Obreimov [13].

The evidence for the presence of very large stress concentrations at the places where elastic twins start is reviewed, and it is concluded that, since the crystal does not fracture, very large stresses must exist locally. For such large strains it is not justifiable to use Hooke's Law, and the non-linear correlation shown in Fig. 21 is assumed to apply. Here η is the relative displacement along the z axis of atoms P and Q of Fig. 20, or any pair of atoms similarly related, and F is the z-component of the force between the atoms. The displacement of atom Q is completed at the twinned position Q'. The idea underlying this correlation is that the twin configuration ($\eta = \eta_3$) is just as stable as, and symmetrical to, that of the parent ($\eta = 0$), and therefore opposite and equal forces are required to move Q towards Q' or Q' towards Q. To make quantitative treatment possible, the solid curve of Fig. 21 is replaced by the dotted line, which has a discontinuity at $\eta = d = \eta_3/2$ to replace the

unstable part of the correlation curve between η_1 and η_2. When $\eta > d$, an « extra twinning force » f acts on atom Q, and an equal opposite force on atom P. In other terms, the z-component of the force on atom Q in its twinned position Q' exceeds by f the force which it would experience if untwinned.

The next step in the treatment is to derive an expression for the Green's funktion $\boldsymbol{u}(\boldsymbol{k})$ of the atom $\boldsymbol{k}$ (i.e. an atom which is at the end of a vector $\boldsymbol{k}$ starting at the origin). $\boldsymbol{u}(\boldsymbol{k})$ is the displacement of the atom $\boldsymbol{k}$ under the influence of *unit* force applied at the origin. This function is expressed as an integral, taken over the unit cell of the reciprocal lattice, of an intergrand involving $\boldsymbol{k}$ and the lattice vibration frequencies associated with each point of the reciprocal lattice (these are, of course, related to the elastic properties of the lattice).

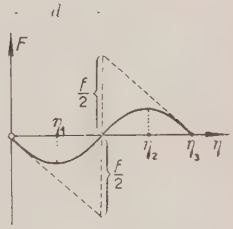

Fig. 21. – Force-relative displacement correlation for pairs of atoms in a lattice capable of twinning. - After Lifšic and Obreimov [13].

Next it is assumed that an elastic twin develops as a monoatomic layer starting from the point of application of the load. A two-dimensional section of the twin taken through this point is considered, so that the following treatment applies to a twin spreading along a single chain of atoms. Before this twin has been formed, the displacement ξ_k of any atom $\boldsymbol{k}$ is given by

$$\xi_k = F \cdot \boldsymbol{u}(\boldsymbol{k}) \,,$$

all displacements, in this simple case, being parallel to the z-axis. Once a twin has been formed and begun to spread along the chain, however, an extra term enters into the expression for ξ_k because of the extra twinning force f acting on each twinned atom. Thus for a given atom $\boldsymbol{k}$, ahead of the twin, the displacement is given by

$$\xi_k = F \cdot \boldsymbol{u}(\boldsymbol{k}) + f\big[\varphi(n, \boldsymbol{k})\big] \,, \tag{1}$$

the second term being the larger, the greater the number n of twinned atoms and the nearer the tip of the twin is to the atom $\boldsymbol{k}$. The function φ is expressed explicitly in terms of the Green's functions of all the atoms in the twin, which can in turn be expanded as a series of integrals.

The authors now derive an expression for the relative displacement η_n (shear) of the leading atom of the twin and its left-hand neighbour. We will call the leading atom « n », because it is defined vectorially by $\boldsymbol{k} = n\boldsymbol{c}$, where $\boldsymbol{c}$ is the lattice period along the z-axis. The left-hand neighbour is defined by $\boldsymbol{k} - n\boldsymbol{c} \quad \boldsymbol{a}$, where $\boldsymbol{a}$ is the period along the x-axis. Another expression

is derived for η_{n+1}, the relative displacement of the next atom $\boldsymbol{k} = (n+1)\boldsymbol{c}$, which has not yet joined the twin, and its left-hand neighbour. Substituting in equn. (1), the second expression is of the form

$$(2) \qquad \eta_{n+1} = \xi_{(n+1)\boldsymbol{c}} - \xi_{(n+1)\boldsymbol{c}-\boldsymbol{a}} = \\ = F\left[\boldsymbol{u}(n\boldsymbol{c}+\boldsymbol{c}) - \boldsymbol{u}(n\boldsymbol{c}+\boldsymbol{c}-\boldsymbol{a})\right] + f\left[\varphi(n, n\boldsymbol{c}+\boldsymbol{c}) - \varphi(n, n\boldsymbol{c}+\boldsymbol{c}-\boldsymbol{a})\right].$$

The particular twin configuration considered will be elastically stable under the applied load F if

$$(3) \qquad \eta_n > d > \eta_{n+1},$$

where d is the critical shear of Fig. 21. If $\eta_{n+1} > d$, then the atom $(n+1)$ will join the twin, and in this way the twin will propagate until the inequality is satisfied.

The best way to appreciate the implications of the theory is to plot the above expression for η_{n+1} graphically. As n increases, the first term will tend to zero, because the Green's functions of two neighbouring atoms become the more nearly equal the further they are from the loading point. This term is represented by curve I in Fig. 22. The second term is the sum of $2n$ Green's functions. When these are all expressed as integrals, it is found that the sum of the integrand tends towards a finite limit. Hence this term is represented by a curve such as II in Fig. 22. η_{n+1} therefore tends towards this same limit, but passes through a minimum first (curve III, given by I + II).

In addition to these three curves, Fig. 22 includes a horizontal line with ordinate $= d$, (IV), and curve V representing η_n, which also tends to a limit as $n \to \infty$. η_n always exceeds η_{n+1}, since it refers to the mutual shear of a pair of atoms closer to the loading point. It is important to notice that curve I is merely one member of an infinite family of curves which are obtained by expanding or contracting I along the ordinates in proportion to the value of the applied force F. The exact height and shape of the curve III is therefore altered as the load is changed.

The inequalities (3) represent the two conditions which must be satisfied if atom n is to be twinned while atom $(n+1)$ is not. For the particular value of F corresponding to curve I as drawn, the second of these inequalities is satisfied for the first integral value of n that exceeds n_m. (Fig. 22). Since $\eta_n > \eta_{n+1}$ always, the first condition will also be satisfied for this value of n. If F is increased, curves II and III are raised and the point m shifts to the right. Physically, this means that more atoms are added to the twin. Eventually, as F is raised further, the whole of III rises above IV so that the second inequality cannot be satisfied for any value of n. This represents the unstable stage at which the elastic twin suddenly turns into a residual twin.

Thus during growth of the twin the dimensions of the twin are always such that d just exceeds η_{n+1}. On the other hand, if an existing elastic twin is unloaded, there is no *change* in dimensions until F has been reduced sufficiently for d just to exceed η_n. This means that curve V must be lowered till the point of intersection P has reached the position m corresponding to the length of the twin at the moment the load began to be reduced. This is a reflection of the fact that there is a range of values of n for which the inequalities (13) are satisfied. Thus we have an explanation of the stress-hysteresis of elastic twinning.

In a further section, the theory is extended to the case where twinning is not restricted to a monoatomic layer. The force is here again assumed to act at a point, and the growth of the twin along all three axes is examined. It is shown that the general analysis given above still applies, and that for a given applied load η_k falls off much more rapidly as the x-coordinate is increased than for increase of the other coordinates. From this it follows directly that elastic twins should always be thin normal to the twinning plane.

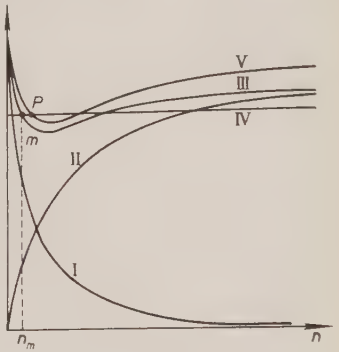

Fig. 22. – Lifšits and Obreimov's displacement functions plotted against the number of atoms in a section of a monoatomic elastic twin lamella. - After Lifšic and Obreimov [13].

It should be noted that it does not follow from the analysis that n_m (Fig. 22) will necessarily increase proportionally with F as F is increased. Indeed, since the curve III has a flat minimum, η_m should increase very steeply with F just before the elastic twin becomes unstable. Thus the observed elastic dependence of twin dimensions on load is not accounted for, but then this experimental law has probably not been verified up to the very last stage of elastic growth. Also the theory predicts that there should be an elastic limit, which Garber did not find; but since the theory is not quantitative, no numerical value for this limit can be derived.

6·3. – *The Theory of Lifšic.*

Lifšic [76] has supplemented the above theory of twinning by a macroscopic treatment in which the crystal is regarded as an anisotropic elastic continuum. A preliminary attempt at such a treatment was made by Garber [17], but it cannot be said that any conclusion of interest emerged from the theoretical part of this paper, beyond the conclusion that certain stresses are discontinuous across the twinning plane of a residual twin. For-

mulae are given for the ratios of these stresses in twin and parent, for the specific case of calcite.

In LIFŠIC's paper a revised stability criterion is used. If μ^P and μ^T are the shear strains (in the twinning plane and along the shear direction) in parent and twin respectively, then the inequalities

$$\begin{cases} \mu^P < \eta_1 \\ \mu^T > \eta_2 \end{cases}$$

must be satisfied if the twin is to be stable (under load). η_1 and η_2 are marked in Fig. 21. It is assumed that η_1 and η_2 are symmetrically disposed, (i.e. $\eta_2 - \eta_1 = \eta_1$). It will be noted that the introduction of *two* critical shear strains marks a departure from the criterion used by LIFŠIC and OBREIMOV.

The other important assumption, taken over from the previous paper, is that for the purposes of tensor analysis the corresponding shear modulus can be taken as constant for all shears, but it is remarked that the value of this mean modulus should be different from the modulus actually found for small shears. It seems to the reviewer that this assumption is the most questionable simplification made in either paper.

LIFŠIC proceeds to calculate the localised force at the twin interface, and finds that its magnitude is fixed but that its direction will depend on the inclination q of the interface to the twinning plane. If q exceeds a critical value $q_{\lim}$ the interface stresses become locally infinite. Moreover infinite stresses arise at the twin «tips» (i.e. the edge of a lenticular lamella) unless the two interfaces meet tangentially. This shape of tip appears to be found in elastic twins in calcite. (This remark is based on an examination of published photographs. Neither LIFŠIC nor GARBER actually say so). It is certainly not true of twins in metals. This disagreement is presumably to be accounted for by the presence of accommodation bends.

In *order of magnitude*, the limiting angle is given by

$$q_{\lim} \sim 2\tau_{cr}/\lambda s ,$$

where τ_{cr} is the «critical» shear stress for creating the twin, and λ is an unspecified mean elastic modulus. (This formula is apparently intended to apply to both elastic and residual twins). Thus small values of the twinning shear s permit large inclinations q and therefore a twin lamella of given area can be thicker for a crystal with smaller s (a prediction made by the reviewer [78]).

More exact formulae show that the limiting angle $q_{\lim}$ is determined, not by s but by $\eta_1 - \eta_2$ (which to a first approximation can be taken as proportional to s for different kinds of crystal). If however the non-linear stress/strain

correlation (Fig. 21) is such that η_1 and η_2 are close together, very large interface inclinations are possible.

LIFŠIC accounts for the results of GARBER *et al.* [16] on the impeding effect of macro-mosaic walls on twin propagation in terms of this limiting angle $\varphi_{\lim}$. Since his analysis also shows that there can be no sudden change in slope of the interface without generating infinite stresses, it follows that a macromosaic boundary of angle exceeding $2\varphi_{\lim}$ should form an impassable obstacle to a spreading twin. For calcite (taking $\tau_{cr} = 1000$ g/mm^2), $\varphi_{\lim} = 10'$. GARBER *et al.* found that the limiting angle for twin propagation across an interface was in the range $8'$ 1°, which agrees in order of magnitude with the calculated $2\varphi_{\lim}$.

It is shown that a stress hysteresis for growth and contraction of a twin also follows from this analysis. Growth will be determined by the condition $\mu^t < \eta_1$, and contraction by $\mu^t > \eta_2$, always assuming that $\varphi \not> \varphi_{\lim}$ as a result of the change of shape of the twin. The analysis is, however, exceedingly intricate.

It is pointed out that the shape is limited by inequalities and not uniquely determined, and that therefore, if the temperature is high enough, the twin may attempt to regain thermodynamic equilibrium. Any small change of shape incurred in this attempt will not necessarily infringe the inequality conditions of mechanical equilibrium. LIFŠIC is very hazy about what constitutes thermodynamical equilibrium, but it is to be presumed that only complete removal of the twin will do, since only this will remove the interface stresses entirely. However, when a twin is thick the intermediate stages of removal might break the conditions of mechanical stability. In this way a start is made towards accounting for the thermal absorption of twins.

The thickening under stress of a residual twin is also analysed. It is concluded that the critical shear stress for this is given by $\tau_g = \lambda' s/2$, where λ' is the effective shear modulus referred to earlier. Thermodynamically, a smaller stress should suffice, and LIFŠIC goes on to suggest that thermal activation could allow a twin to grow gradually under a constant stress τ smaller than τ_g. In this way THOMPSON and MILLARD's [27] «twinning creep» can no doubt be accounted for. The frequency of the thermal fluctuations determining such twinning creep depends on the value of τ (and of course on the temperature), and if these are high enough, the resultant K.E. of the boundary may suffice to promote an avalanchelike growth of the twin. It is stated that GARBER in his Dissertation reported such behaviour, and that it always led to the destruction of the specimen.

One thing which is not clear from the analysis is what state of stress is set up when a lenticular twin in a metal is absorbed by the parent on annealing. The tips of the lamellae are blunted, and by all the above considerations the crystal should break there; but this is not observed to happen.

The conclusions of both the papers discussed are of the greatest interest, but it must be remarked that the mathematical argument is often exceedingly obscure or abbreviated and the notation sometimes either unexplained or altered without notice. It is to be hoped that someone will now attempt to extend these theories to further unsolved problems, such as a detailed analysis of twin absorption and the influence of accommodation bending.

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Recent Soviet Work in the Field of Crystallography.

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(ricevuto il 24 Giugno 1953)

CONTENTS

1. The Position of Crystallography in the Soviet Union. - 2. Sources and Bibliography. – 3. Historical, Instructional and Review Material. – 4 Symmetry and Structure Determination Theory. – 5. Structures. – 6. Instruments, Apparatus and Practical Techniques. – 7. Electronography. – 8. Crystal Physics. – 9. Crystal Chemistry. – 10. Growth and Textures. – 11. Metals. – 12. Conclusions. – 13. Aknowledgements. - 14. Bibliography.

For as the proficience of learning consisteth much in the orders and institutions of universities in the same states and kingdoms, so it would be yet more advanced, if there were more intelligence mutual between the universities of Europe than now there is.

FRANCIS BACON, *The Advancement of Learning*, 1605.

1. – The Position of Crystallography in the Soviet Union.

Crystallography is one of the sciences in which, through the work of FEDOROV, GADOLIN, VULF and their schools, Russia had achieved eminence in pre-Revolutionary times. The early traditions have, to some extent, continued as research turned, from being purely academic, to include industrial objectives [14]. For example, the Memoirs of the All-Union Mineralogical Society have been published continuously since 1866. The effects of the late war have now largely passed and the quantity and quality of papers steadily increases with the encouragement of the government and the Academy of Sciences. N. V. BELOV was awarded a first-class Stalin prize for his structural crystallography in 1951 and the FEDOROV prize of 10000 roubles is offered in 1953 for the best work in the subject. Since the war there have been four All-Union conferences [1-4] for the application of X-rays to the study of materials, the last (in 1952) being attended by 595 delegates. Besides the Insti-

tute of Crystallography and the Fedorov Institute, there are chairs of crystallography at Moscow, Leningrad, Gorki, and Lvov Universities [8]. The number of papers published annually in national journals can be estimated at about 100. It is noteworthy that more than one fifth of the authors of papers are women.

2. – Sources and Bibliography.

There is no current Soviet abstracting or referencing journal [F1], although the newly organised Institute of Scientific Information is due to begin publishing one in 1953 [5], and therefore papers have to be found from the original journals or from foreign abstracts. A list of references is published in the *Journal of Technical Physics*, but this is often inadequate. Only certain journals, which vary from year to year, are available for foreign subscription and any others can only be obtained by exchange [6] or through diplomatic channels. The periodical holdings of the British Museum itself have deficiencies, and the general position as regards the availability of even the common journals is poor, apparently more as a result of organisational failings, than of an official policy. Abstracting in Britain is by no means complete, and looking through the runs or indices of the actual periodicals is the only certain way of ensuring a reasonable coverage. It is estimated that the bibliography of the present review is more than 90 % complete, except perhaps in borderline papers. The Library of Congress Monthly List of Russian Accession giving contents lists (since 1952 classified by subjects) is probably the most useful non-Russian publication for locating papers.

Papers on crystallography may appear in any of the journals on physics, chemistry or mineralogy, or any of the university journals. The only periodical devoted entirely to crystallography is the *Transactions of the Institute of Crystallography*, which has changed its name several times with that of the Institute as the latter expanded [7].

Because of the mass of material this review is confined (except in the case of work in unfamiliar publications) to papers published during and after 1950. Papers covered by *Structure Reports* (which have now reached 1949) are omitted. Those papers and books which could not be located are marked, with an asterisk. References to theses are not given, because, although abstracts may be available, it is unlikely that the originals could be consulted. Many papers are listed but not explicitly discussed, as their titles seem sufficient indication of their contents. Where abstracted by *Physics Abstracts* the number and date of the abstract is given.

3. – Historical, Instructional and Review Material.

Contemporary Russian science is very conscious of its historical origins and much research and popularisation work is done concerning early scientists. Definitive editions of the collected works of Fedorov [9, 10] and of Vulf [15, 16] have been issued.

To make recent expansions of the use of crystallography in industry possible, many textbooks [17] have been published and are interesting because they make possible some assessment of the state of development of the science. Translations have been made of numerous standard English language textbooks [18] so that the teaching institutions must be well provided with material. Bokij and Poraj-Košic book might be singled out for special mention as an excellent and original textbook. It is based on lectures given in the Geological and Chemical Faculties of Moscow University. The first volume (the only one yet to appear) covers: I, « Fedorov's theory of the structure of crystals », including a section of the International Tables for 30 important space groups – an explanation of space group theory; II, « X-rays and crystals »; and III, « The first stage of a structure analysis » (investigation of symmetry and lattice type) – a description of various cameras and what can be done with them [F16].

At a more advanced level, examination of reviews of various topics give Russian opinions of their own progress, but most reviews are not confined to Russian work. A most comprehensive review of neutron diffraction work refers almost entirely to foreign papers [13].

4. – Symmetry and Structure Determination Theory.

A. V. Šubnikov, Director of the Institute of Crystallography, has himself specialised in the study of symmetry [43-47] and in 1946 compiled an atlas of space groups [43]. N. V. Belov demonstrated at length how the space groups can be derived by elementary methods from the 32 point groups [22]. A considerable number of papers on aspects of symmetry have been produced by these two authors, but the majority are didactic or explanatory in nature, elucidating, rather than discovering anything new. For an understanding of the style of many Russian papers on structures, an examination of Belov's frequently quoted book [19] on the geometry of ionic structures is essential, and explains the emphasis on « geometrical » analysis. The detailed consideration of the packing of linked polyhedra stems directly from Fedorov's work.

As an example of the reasons for the reliability of the work of Belov's group the examination of the Patterson-Harker method by Belov and Mo-

KEEVA [26] might be cited. In this extended test 22 known structures, having one or two parameters, were redetermined by calculating Patterson-Harker lines. The structure amplitudes were obtained from powder photographs. The agreement with the accepted parameter was good in all but three cases.

An interesting speculative excursion was made by V. I. MIHEEV [35-37] who introduced generalised symmetry planes which reflect obliquely, transforming a sphere into an ellipsoid, and discussed the resulting homology space groups. ŠUBNIKOV [48] points out that this theory has no relevance for real crystals.

Special cases of soluble structures have been discussed [27, 42], but the general theory of phase determination has not received as much attention as elsewhere, although one most important paper [62] applies Harker-Kasper inequalities very successfully. ZVONKOVA and ŽDANOV [51] have also begun to use inequalities, deriving an expression for phase relationships similar to that found by ZACHARIASEN [F2].

Other aspects of structure analysis, solution from the Patterson function [32], termination errors, accuracy of coordinates [30] and detection of centrosymmetry [31], have been considered by KITAJGORODSKIJ, who discussed the latter point with A. J. C. WILSON [F3]. Statistical methods of putting intensities on an absolute basis, refinement of coordinates by least squares and other modern techniques have been used at the Institute of Organic Chemistry [76].

KITAJGORODSKIJ's textbook which includes these topics is a remarkably complete treatment of the whole of crystallography (excluding crystal physics and chemistry). It covers optical and geometrical crystallography, symmetry theory, practical single-crystal techniques, summation techniques and packing theory, and contains examples of structure determinations of varying degrees of complexity [F16].

Except in detail, structure determination techniques do not add to what is known outside Russia.

5. – Structures.

There appear to be at least two main schools of crystallography concerned with structure determination. N. V. BELOV at the Institute of Crystallography specialises in complex silicates [8]. Some of his work has confirmed or revised pioneer determination of the structures of beryl [F4, 54, 60], olivine [F5, 57] and dioptase [F6, 61]. By coincidence it has happened that several other structures have also been worked out independently and simultaneously by American and Japanese groups. For tourmaline there are slight differences between the final atomic positions found by BELOV [52] and by DONNAY and BUERGER [F7] although their experimental data were identical [55], and de-

tailed criticism will be necessary for a definite decision either way. Belov [53, 56] agrees [90] with Ito and his co-workers [F8] on the structure of milarite, the existence of a new silicate anion of formula $Si_{12}O_{30}$ being proved. Japanese work on ilvaite [F9] is severely criticised and the correctness of the Russian work [58] is maintained by the authors [59].

Belov and Rumanova's determination of the structure of epidote [62] is of great importance. Unfortunately their account appears as yet only in *Doklady* where all papers are limited to four pages and only results with a brief outline of methods are given. The unit cell of epidote is monoclinic ($P2_1/m$) with $b = 5.62$ Å and 350 hol reflections were measured. The strict application of inequalities followed by Zachariasen's averaging method gave the signs of 295 of these reflections and the subsequent Fourier projection (fig. 1) showed all the atomic positions. Both Si_2O_7 and SiO_4 groups are found making the structure of special interest. This must be one of the few determinations of complex silicates made without a model, and therefore it provides a datum point in silicate chemistry. It represents the best work yet done by Soviet crystallographers.

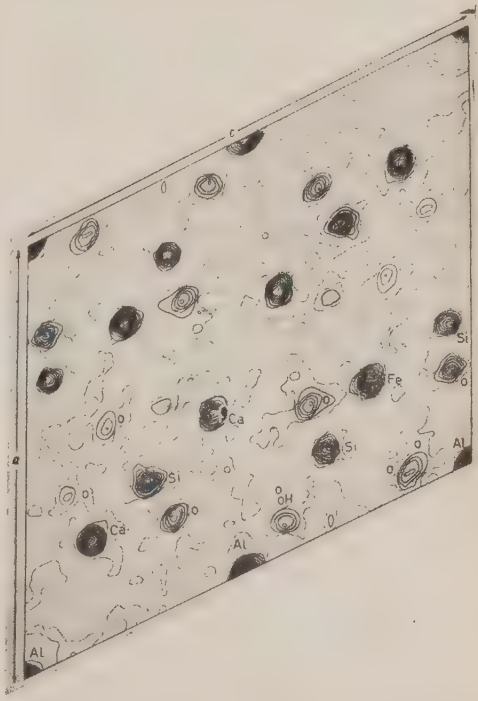

Fig. 1. – 010 Fourier projection of epidote using phases obtained from inequality relations.

Professor G. S. Ždanov's group at the Karpov Physico-chemical Institute have examined a series of thiocyanates [100, 102, 105-109] and agree substantially with Jeffery [F10] and Scouloudi [F11] on the constitution of the mercury thiocyanate group. Metallo-organic compounds [77, 80, 81, 96, 99] and compounds of gold [97] and platinum metals [64, 66, 91-93] have been studied considerably, being particularly suitable for X-ray analysis. For historical reasons also precious metal compounds receive much attention. As stereochemical rather than

crystallographic aims are paramount, accuracy has been to some extent sacrificed to quantity and atomic coordinates are not always very precise.

Other structures fall into no definite scheme, being examined by separate institutes for different reasons, but there is a definite tendency towards the extensive method — the examination of several structures in outline [73-74], rather than the determination of any one structure by itself. Packing considerations, often unconfirmed by intensity work, are used wherever possible, rather than more sophisticated methods of phase determination. There is no evidence that electronic, optical or punched card methods of computation are in use and the general impression is that, particularly in those laboratories which are not primarily crystallographic, techniques of analysis are somewhat behind those used in Britain and America.

6. – Instruments, Apparatus and Practical Techniques.

A complete range of X-ray diffraction cameras has been made by the Physics Scientific Research Institute of Moscow University under the direction of M. M. Umanskij. In publications the instruments are often referred to by their initials only, which therefore follow their descriptions. The range comprises:

(*a*) A powder camera (about 5.7 cm diam.) something like the North American Philips product (RKD);

(*b*) An 11.4 cm diameter powder camera for precision work. The maximum recordable θ-value is 87° (RKU) [114];

(*c*) A semi-focussing powder camera needing exposures of less than 10 minutes (RKE) [123];

(*d*) A conventional design single crystal goniometer for oscillation or rotation photographs. Provision is made for a flat film to lie on top of the cylindrical film cassette to record all layer lines up to $\zeta = 1.0$ and this technique is sometimes used (RKV) [compare F12];

(*e*) A flat plate camera for Laue photographs — both high and low angle reflections can be recorded (RKSO);

(*f*) A single crystal camera for oscillation photographs specially modified for obtaining layer lines for unambiguous determination of cell repeat distances. Although the axis of oscillation coincides with the axis of the cylindrical film holder, a large arc permits the mounting axis of the goniometer head to be rotated up to 90° away from the oscillation axis for the determination of all dimensions and angles without remounting the crystal (RKOP) [compare F13];

(*g*) A Weissenberg camera of normal design – sometimes non-standard ratios are used (RGNS);

(*h*) A de Jong and Bouman camera, used increasingly by Umanskij for the photography of the reciprocal lattice (KFOR) [112].

Elsewhere, a Sauter goniometer of German design made by LITMO is in use and also an X-ray spectrograph with proportional counter, which seems adapted for the equatorial layer line only. Leningrad University use a 14.33 cm diameter precision powder camera of high resolving power (VRS-3-LGU).

X-ray tubes are more or less conventional except for a fine focus tube developed by Professor B. Ja. Pines' group at Harkov [110]. The electron image of a small hairpin filament is focussed by means of the field at the anode, which is the point of a cone of semi-vertical angle 70° (Fig. 2). A special feature, which is said to give increased efficiency, is that the beam emerges normally from the target surface, instead of at a glancing angle of about 5° as is usual. The tube appears in a number of modifications for different uses. A spot area of 0.005 mm² and a loading of 8 kW/mm² is achieved. This compares with 0.0016 mm² and 11 kW/mm² for a British tube with a different type of focussing [F14].

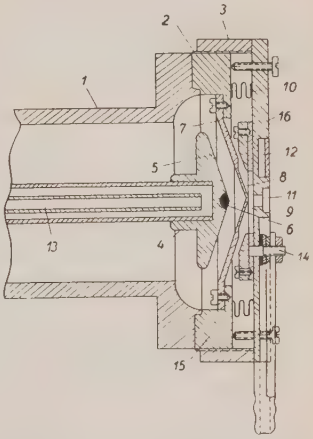

Fig. 2. – Schematic drawing of fine-focus X-ray tube with adjustable focus.

1. Tube body.
2. Plane section.
3. Adjudsting screw.
4. Anode.
5. Focussing anode surface.
6. Working part of anode.
7. Focussing cathode cone.
8. Nickel cap.
9. Filament.
10. Syphon bellows.
11. Window.
12. Channel for cooling cathode.
13. Tube for cooling anode.
14. Terminal.
15. Washer.
16. Disc.

E. E. Flint's examination [117] of the technique for the optical goniometry of crystals may have some importance now that the Barker Index is available. The accuracy of two-circle goniometers of various design is calculated as it changes with the angular settings.

7. – Electronography.

The field in which the most original work has been done is undoubtedly that of the application of electron diffraction to crystal structure. Tartakovskij in the USSR began to publish papers only a year after the original paper by Davisson and Germer, and the theoretical possibility of locating the hydrogen atoms in NH_4Cl was realised practically in 1933 by Laškarev and Usyskin. Figure 3 shows a section through a CH_2 group in a paraffin from a recent analysis [145, 147]. Only lately has this technique been applied elsewhere [F15] (to show the hydrogen bonding in H_3BO_3).

The important preliminary work of obtaining reliable atomic scattering

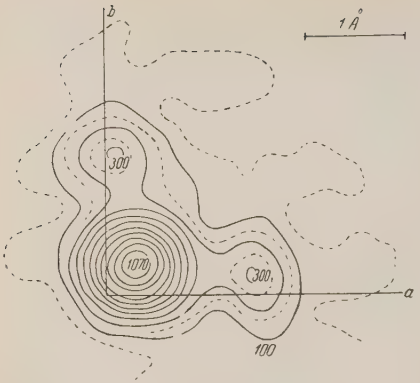

Fig. 3. – Three-dimensional Fourier synthesis at a height $^3/_4\,c'$, giving a map of the potential distribution in a CH_2 group. Contours are at arbitrary intervals of 100 units.

curves for electron waves was carried out in a particularly thorough way by JAMZIN [134]. The expected value for the electron scattering factor of $k(Z - f_x)\lambda^2/\sin^2\theta$ was found to obtain but there were slight corrections. During this work the apparently simple, but practically rather difficult, problem of measuring relative intensities of diffraction lines and spots was solved by taking series of photographs with different exposure times on the same plate and matching lines of nearly equal intensity. Blackening curves of electrons of different energies were measured. The tech-

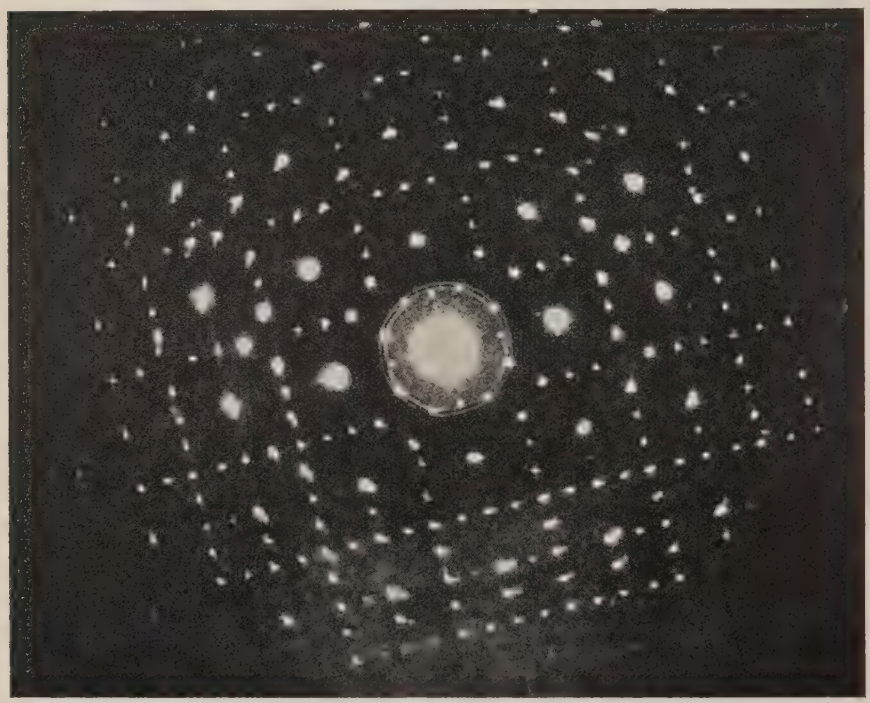

Fig. 4. Electronogram from $BaCl_2 \cdot H_2O$.

nique has gradually improved until accurate intensities can be obtained from powders, oriented texture [149, 150], and single crystals for use in Fourier summations in the usual way.

The advantages of electron diffraction may be listed briefly:

(*a*) A Fourier synthesis with scattered amplitudes shows the electric potential distribution in the unit cell. As the corresponding X-ray map gives electron density, great possibilities are apparent for the observation of the electrical forces in crystals and the electronic configuration of bonds.

(*b*) As electronic and X-ray scattering curves are different, possibilities for phase determination exist, rather as in the case of isomorphous replacement.

(*c*) Very low and very high atomic number elements are not as different in scattering power from medium atomic number elements as in the case of X-ray scattering.

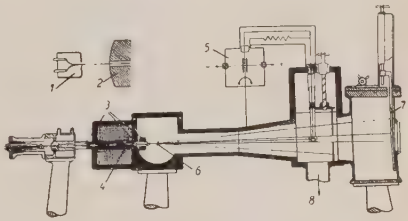

Fig. 5.

Diagrammatic section of electronograph.

1. Cathode.
2. Anode.
3. Diaphrams.
4. Lens.
5. Electrometer.
6. Specimen.
7. Plate.
8. Pump.

(*d*) An electron beam is easily monochromatised to any convenient wave length.

(*e*) The results of moving the specimen are immediately apparent on the fluorescent screen as intensities are perhaps 10^5 times greater than those used in X-ray diffraction. Rapid changes can therefore also be followed.

(*f*) Single crystal photographs can be obtained from crystals only a few hundred Ångstrom units in size; indeed such small crystals are necessary to prevent complicating effects due to multiple diffraction.

At present the disadvantages are largely experimental but Professor PINSKER and his group are continually improving their technique. PINSKER's book [136, 153] gives a comprehensive account of the work done up to 1949.

A special study has been made of the AX_2-type halides and their hydrates, some of which were not previously known, and the results seem quite comparable with those of X-ray analysis [143, 146, 151]. Figure 4 shows the diffraction pattern from $BaCl_2 \cdot H_2O$ [136]. More difficult materials, such as clays [137] which cannot be obtained as large crystals and polymer films [133] are now being examined. The investigation of surface layers of oxydes [140] and deposited metals [148] has proceeded, but this application is well known elsewhere. Figure 5 shows a diagram of the apparatus used by PINSKER's group [134].

8. – Crystal Physics.

A large number of papers on $BaTiO_3$ and other ferroelectrics have been excluded from this list as they are not of purely crystallographic interest. Most of the papers quoted need no further explanation than is provided by their titles and fall into no well defined groups, except for a number of mathematical studies of systems of coupled oscillators from which can be calculated the thermal capacity and various mechanical properties of certain idealised structures [176, 183, 185, 187-189]. In some cases useful information of crystallographic importance can be obtained. For example it is concluded that wollastonite, $CaSiO_3$, does not have a chain anion structure but that its observed specific heat is consistent with the presence of Si_3O_9 rings [184]. The melting range of a linear polymer is given a successful quantitative explanation in terms of rotation of its links as an order-disorder phenomenon [190].

Several attempts have been made to determine the electron distribution in various types of bonds in very simple compounds and, although the results are open to criticism, it was shown that the electron density is increased along the tetrahedral bonds in diamond and in the cube directions in aluminium [165].

It might be noted that Hristov, who discussed mathematically the physical process of the diffraction of X-rays by an array of oscillators [164], is a Bulgarian contributor to *Doklady Akademii Nauk SSSR*. (See *Crystallography in Eastern Europe*, pag. 415 of this *Supplemento al Nuovo Cimento*).

9. – Crystal Chemistry.

X-ray crystallography has been applied in industry to an increasing extent, mostly for the identification of compounds, such as in boiler scale and in various catalysts [195, 205, 209]. However, most of the papers collected into this section describe attempts to interrelate the results of X-ray analyses and describe structures in terms of interatomic forces. In ionic structures, atomic radii and coordination numbers are the simplest parameters and suitable structures are examined in this way [199, 202] regularities being explained in terms of Pauling's rules. The way in which ions of charge one or three can replace Ca and Mg ions in silicates is discussed by Tauson [207], and Belov [197, 198] has examined qualitatively similar changes where replacements in glasses lead to devitrification and in feldspars to the appearance of a whole range of minerals. Avgustinik's book [196] gives an excellent account of the crystal chemistry of the silicates. Except in detail little of the work will appear unfamiliar.

10. – Growth and Textures.

The principal industrial tasks given to the Institute of Crystallography have been concerned with growth and texture [16]. They include the preparation of synthetic rubies for bearings, of abrasive and cutting materials [216, 230] and of crystals, natural and synthetic, for piezoelectric devices [219-222, 232]. Several papers are concerned with the problems arising in this programme.

The production of a uniformly grained syntehtic corundum (grain size 3-5 microns) for metal cutting at speeds up to 2 000 m/min is reported [237]. Cast iron was the material cut at this speed.

LEMMLEJN has extensively studied a case of crystal growth where the conditions of crystallisation are especially closely circumscribed. He examined the migration of « negative crystals » – inclusions of mother liquor bounded by faces, in large crystals, as material was dissolved at the hotter side of the cavity and deposited at the colder. Although his papers are almost entirely descriptive, the arrangement seems peculiarly suitable for quantitative work [242, 244, 245].

Of particular interest are a series of papers by KAPUSTIN [233-236], again mostly qualitative, on the influence of ultrasonic waves on crystallisation, transformation and solution processes. The rate of nucleation, both in melts and in solutions, is increased and an ultrasonic field has been applied industrially to increase the uniformity of grain size and texture in solidifying melts of non-ferrous metals. In a standing wave field the resulting solid may show marked bands coinciding with nodes and antinodes. The rate of solution of crystals may be increased up to 20 times and the rate of polymorphic transformation can also be accelerated. Glasses can be devitrified.

An extensive and thorough test of the Donnay-Harker principle, substantially confirming its validity, has been made by ŠAFRANOVSKIJ [251].

11. – Metals.

It is hardly possible to discuss any topic in metallurgy without considering the state of crystallisation of the metal but only papers involving X-ray crystallographic work have been selected for consideration.

The structures of a few intermetallic compounds, Cu_2Cd [291], $AlAu_4$ [292], and Cu_4MgSn [281] have been determined but the most important subjects studied are those of direct practical use. The martensite-austenite transformation in steel [266-268] and the process of ageing in aluminium alloys [269-272, 277-279] have been intensively studied by several institutes and factory laboratories. BELOV [273] has suggseted that Fe_6C has a structure

like that of U_6Mn which would enable carbon to dissolve in γ-iron without increasing the cell size significantly, and that local order in austenite has this structure.

Bagarjackij [271], using monochromatised radiation and a de Jong and Bouman camera, examined the pseudo-binary alloy Al–AL_2CuMg as the latter phase separated, explaining the crystallite orientation in terms of atomic structure. Metal physics received considerable attention and a neat apparatus was constructed by Hotkevič [286] for compressing a metal specimen at liquid air temperature and taking X-ray photographs of the deformed metal at that temperature. The structure of lithium metal on deformation at 20° K changes from body-centred cubic to face-centred cubic.

The carbides used for high speed working of metals form a field where investigation may be at once repaid by practical results [276, 305].

X-ray methods of strain determination are used widely [304, 306].

12. – Conclusions.

Crystallography has always been one of the sciences where foreign work has been closely followed. The simultaneous discoveries of Barlow, Fedorov and Schoenfliess ensured the wide diffusion of the fundamentals, and the immediate intelligibility of results, which were perhaps only reached by intricate reasoning and enormous calculation, contributes to the rapid flow of ideas. Publication of the Structure Reports both demonstrates and increases the essentially international nature of the subject. It might be mentioned that the International Union of Crystallography has its « instructions to authors » printed in Russian hopefully reproduced in every copy of *Acta Crystallographica*. It has been the aim of this review to demonstrate the truth of Bacon's observation that an increased exchange of information would be mutually advantageous.

13. – Acknowledgements.

Thanks are due to Professor J. D. Bernal for encouraging the production of this article, and to the librarians of the Slavonic section of the British Museum and of the Russian Union Catalogue of the National Central Library for their help in its compilation.

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Crystallography in Eastern Europe.

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The countries to be considered are Albania, Bulgaria, Czechoslovakia, Hungary, Jugoslavia, Poland and Rumania. All have followed a common pattern of scientific, as well as historical, development. Having served as sources of raw materials for more industrialised states, their universities have long-established mineralogical departments. They are still not very advanced, however, in the experimental-inductive, as contrastred with the classificatory and descriptive, branches of science. The few workers who have studied crystallography have had to learn foreign languages and go abroad. Continuing their work after returning home, they send their best papers to the international journals in the languages of their teachers. Papers of secondary importance, also written in major languages, appear in national journals. The only papers in national languages are either translations of papers published elsewhere, or relatively minor contributions. A survey of *Acta Crystallographica* and the major Russian periodical publishing crystallographic papers should therefore cover the work of the above-mentioned countries, and, for crystallographic purposes, their national languages need not be considered.

The recent reconstitution of several Academies of Science with executive powers on the pattern of the Soviet Academy, together with the general increase in scientific activity, may be expected to alter this situation in a few years.

Travaux soviétiques sur la théorie de la liaison chimique.

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SOMMAIRE

1. Introduction. – **2. Période 1947-1950.** 1. Generalités. 2. Molécules diatomiques. 3. Molécules compliquées. – **3. Ions complexes.** – **4. Période 1950-1952.** 1. Critiques de caractère empirique. 2. Objections théoriques. 3. Objections philosophiques. – **5. Période 1952-1953.**

1. – Introduction.

Nous avons pris comme date de départ de cette revue bibliographique l'année 1947, car on peut considérer que le livre de SYRKIN et DJATKINA, *Structure des molécules* [1], rend compte d'une manière satisfaisante des travaux antérieurs des savants soviétiques (*).

Les années qui suivirent peuvent être divisées en trois périodes distinctes:

— l'une de 1947 à 1950, pendant laquelle les conceptions de la théorie de résonance ont dominé les travaux des chercheurs soviétiques, si l'on fait abstraction des critiques très discutées d'ailleurs de ČELINCEV [2] et de RAZUMOVSKI [3];

— la deuxième (1950-1952) qui est une période de crise et de discussions parfois violentes, culminant dans la « Conférence sur le stade actuel de la théorie de la structure chimique en chimie organique » [4], organisée par l'Académie des Sciences de l'URSS (Moscou, Juin 1951); et enfin

— la troisième, débutant en 1952, qui est caractérisée par des tentatives d'édification d'une théorie de la structure et de la liaison chimiques sur des bases nouvelles.

(*) A une exception près, tous les travaux cités ont été effectués en URSS.

2. – Période 1947-1950.

2·1. – *Generalités.*

Bočvar [5] a donné une bonne mise au point de la théorie de superposition de structures (ou de résonance). Il distingue la « méthode de résonance » et le « principe de résonance ». La méthode de résonance est un cas particulier de la méthode de variation où la fonction d'onde (f.o.) φ a la forme d'une combinaison linéaire de certaines f.o. approximatives, φ_i données, les paramètres λ_i étant leurs coefficients.

Si les fonctions φ_i sont des fonctions stationnaires, choisies de telle sorte que chacune d'entre elles décrive une structure chimique imaginable et physiquement interprétable, ou un état, la fonction φ correspondra à una superposition d'états. Le principe de résonance postule que l'état réel de la molécule exprimé en termes d'états de valence des atomes et du système de liaison, ne peut être exactement représenté par aucune formule structurale isolée; une description plus proche de la vérité est celle d'un hybride d'états représentés par des formules de structures possibles. Toutefois, il faut se garder de plusieurs interprétations fausses souvent proposées:

a) L'état de superposition n'est pas un état « mésomère » ou intermédiaire, car d'une part la f.o. « totale » φ ne possède pas en un point donné de l'espace de configuration, une valeur intermédiaire entre la valeur maximum correspondant à une f.o. composante φ_i et la valeur minimum correspondante à une autre f.o. composante φ_j. D'autre part, si certaines grandeurs physiques mesurables telles que les longueurs de liaison, la fréquence de vibration, le moment électrique, sont intermédiaires entre celles des « états » composants (propriétés « meso »), d'autres, l'énergie de liaison en particulier, ne le sont pas.

b) L'état de superposition est un état stationnaire, possédant une énergie bien déterminée. Il est donc faux de considérer la superposition comme une description d'une variation périodique s'éffectuant à une grande vitesse et consistant dans le passage du système d'un état composant à un autre.

c) L'état de superposition ne correspond pas à une tautomérie, « électronique » ou autre, car ceci conduirait à admettre pour un ensemble de molécules, l'existence à chaque instant de molécules correspondant aux différentes structures en équilibre thermodynamique ou encore, qu'à un moment donné, l'état d'une molécule correspond à une structure composante déterminée.

Bočvar [6, 7] a etabli en outre quelques théorèmes généraux interessant la méthode de superposition de structures.

Kovner et Sverdlov [8] ont proposé une méthode simple, consistant en

une généralisation de la méthode graphique de Rumer [9] pour la construction d'un système canonique permettant de calculer les états triplet des molécules compliquées.

Blumenfeld [10] a donné une formule générale permettant de calculer le nombre N d'états singlet de molécules compliquées. Si $2n$ est le nombre d'électrons délocalisés et K celui des centres ayant un électron supplémentaire, on trouve, tant par la méthode L.V. (*) en tenant compte de structures ioniques que par la méthode O.M. (*) en considérant les fonctions d'état antisymétriques, que:

$$N = (2n)! \sum_{k=0}^{n} \frac{1}{(k!)^2 (n-K)!\,(n-K+1)!}\,.$$

Kapustinskij [11] a donné une nouvelle définition de l'électronégativité, valable pour les cristaux, et a montré que les valeurs des électronégativités auxquelles elle conduit permettent de calculer la chaleur absolue de formation des cristaux ioniques.

2·2. – *Molécules diatomiques.*

Vesëlov et Adamov [12] ont utilisé une méthode de variation pour calculer la polarisabilité de la molécule H_2 en se servant d'une fonction d'onde pour la liaison homéopolaire à laquelle on ajoute deux termes ioniques avec les poids indiqués par Weinbaum [13]. La polarisabilité moyenne et l'anisotropie calculées ainsi, sont en bon accord avec les données expérimentales. Adamov [14] a utilisé le même procédé pour calculer la variation de la polarisabilité parallèlement et perpendiculairement à la direction de la liaison en fonction de la distance internucléaire. Ceci lui a permis de calculer la dépolarisation $\varrho_{calc} = 0{,}05$ de la raie Raman, en meilleur accord avec la valeur expérimentale (0,06) que la valeur calculée par Hirschfelder [15] ($\varrho_{calc} = 0{,}01$).

Adamov [16] a étudié la nature de la liaison et a calculé le moment dipolaire de la molécule LiH, en admettant une superposition d'une liaison covalente et d'une liaison ionique. La configuration électronique de cette molécule permet d'utiliser les formules correspondant à une séparation incomplète des variables [17]. En prenant la distance internucléaire expérimentale l'auteur trouve que la contribution ionique est de 34%, toutefois l'énergie de liaison calculée ne représente que 60% de la valeur expérimentale. Le moment diélectrique calculé est de 1,34 D, dont 0,34 D proviennent de l'assymétrie du nuage électronique.

(*) L.V.: liaison de valence; O.M.: orbitales moléculaires.

Cicišvili [18] a calculé l'énergie, la distance internucléaire et les fréquences de vibrations qu'auraient les molécules HF et HCl si les liaison étaient purement ioniques et les a comparées aux valeurs expérimentales. Les distances internucléaires calculées ainsi sont sensiblement (20-30 %) trop grandes, tandis que les fréquences sont trop faibles. Ceci permet de prévoir le sens de variation de ces grandeurs, quand on passe des molécules gazeuses aux molécules dissoutes dans les solvants ionisants.

Nekrasov [19] a montré qu'en admettant pour CsF la superposition d'une liaison simple et d'une liaison semi-polaire, et en adoptant les valeurs de l'électroaffinité de l'auteur [20], il était possible de rendre compte du moment électrique de cette molécule.

2·3. – *Molécules compliquées.*

Djatkina [21] a calculé l'énergie de résonance des hétérocycles à 6 atomes contenant de l'azote iminique. Un des atomes d'azote est trivalent et électriquement neutre, l'autre bivalent et négatif. Les méthodes habituelles (O.M. et L.V. (*)) peuvent être utilisées à condition de tenir compte du fait que:

a) l'énergie coulombienne de l'électron est plus élevée au voisinage de l'hétéroatome qu'au voisinage d'un atome de carbone et que

b) l'énergie d'échange de l'hétéroatome avec le carbone est plus élevée que celle existant entre deux atomes de carbone.

Dans la méthode O.M., on est ainsi conduit à introduire deux paramètres supplémentaires δ et γ.

Dans la méthode L.V., on tient compte de *b*) en donnant à l'intégrale d'échange C-X, une valeur plus élevée qu'à l'intégrale C-C correspondante.

Pour les hétérocycles contenant de l'azote, l'introduction de δ conduit à une certaine diminution de l'énergie de résonance par rapport aux hydrocarbures correspondants. Comme pour les noyaux phényliques condensés, on trouve pour des hétérocycles condensés des énergies de résonance différentes pour les différents isomères (se distinguant entre eux par le mode de condensation et la position des atomes d'azote), selon le « poids » des liaisons « longues » vers le hétéroatomes.

Bagdasarian [22] a utilisé la méthode L.V. pour calculer l'énergie de conjugaison (ou de résonance) ainsi que les positions de états excités pour le benzène, le radical allyle, le butadiène, l'hexatriène, l'octatriène, le naphtalène, le styrolène, le graphite et une chaîne conjuguée infinie. Pour calculer l'énergie de liaison en fonction de la distance il a utilisé en la modifiant la méthode de Lloy et Penney [23]. Il a attiré en particulier l'attention sur

l'impossibilité de se servir des fonctions de Morse expérimentales pour la liaison localisée, car il s'agit de liaisons fictives, n'existant pas dans la nature.

Davidov [24] et Blumenfeld [25] ont calculé les positions de premiers niveaux excités du naphtalène, le premier par la méthode O.M., le second par la méthode L.V. Davidov a obtenu les règles de sélection, la polarisation et la force des oscillateurs pour les transitions correspondantes, en tenant compte de la non-orthogonalité des fonctions d'onde d'atomes voisins.

Blumenfeld [26] a contesté la possibilité d'utiliser la méthode O.M. pour calculer les transitions singlet-singlet. Davidov [27] dans sa réponse fait ressortir l'importance de la correction pour la non-orthogonalité et sur l'accord de ses calculs avec l'expérience.

Blumenfeld [25] a tenu compte dans son calcul des 42 structures canoniques du naphtalène, et il a montré que la théorie de groupes permettait de réduire l'équation séculaire du $42^{\text{ème}}$ degré à 4 équations du $16^{\text{ème}}$, $10^{\text{ème}}$, $10^{\text{ème}}$, et $6^{\text{ème}}$ degré respectivement. Il a montré d'ailleurs par la suite [28] qu'il existait une méthode générale pour effectuer de telles réductions lorsqu'on tient compte de la symétrie de la molécule; cette simplification lui a permis de calculer les positions des niveaux singlet du styrolène. Dans le cas du naphtalène il a pu établir la position des 5 premiers niveaux avec une meilleure précision que Forster [29] qui n'avait tenu compte que des structures de Kekulé. L'accord avec l'expérience est excellent: 3 177 Å calc. contre 3 193 Å observé et 2 889 Å calc. contre 2 820 Å observé.

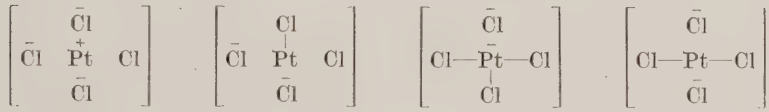
Per contre on ne prévoit pas de transition pouvant donner naissance à la bande très intense, située à 2 209 Å et qui correspond à la bande 1 850 Å du benzène. L'auteur suggère qu'il s'agit dans ces cas de bandes provenant de l'excitation des électrons participant à la liaison C—H.

Davidov [30] a calculé, par la méthode L.V., le spectre d'absorption de la molécule du diphényle en étudiant le dédoublement des niveaux énergétiques des groupes phényles, ainsi que la variation de la fréquence d'absorption des parapolyphényles avec le nombre de groupes phényliques [31].

3. – Ions complexes.

La nature de la liaison chimique dans les ions complexes a été examinée par Syrkin [32]. Selon cet auteur il n'y a aucune différence de nature entre les liaisons dans les ions complexes et les liaisons ordinaires, mais seulement une différence de degré; dans les complexes, la délocalisation joue un rôle très important, le nombre de coordination pouvant être plus grand que le nombre d'électrons de valence normaux. L'interprétation électrostatique de ces liaisons est fausse. On ne peut admettre, par exemple, l'existence de Pt^{++} (Pt divalent s, d) dans le complexe K_2PtCl_4, car le diamagnétisme de l'ion $(PtCl_4)^{--}$ est

inférieur à celui de 4 ions Cl , ce qui exclut la présence d'ions Pt^{++} [33]. De même, le diamagnétisme des liaisons Pt—Br dans $(PtBr_4)^{-}$ et des liaisons Pt—I dans $(PtI_4)^{--}$ est inférieur à celui de 4 ions Br^- et de 4 ions I^- respectivement. Il n'existe par conséquent pas dans ces ions complexes d'ions simples d'halogènes. De même la conception strictement covalente où l'atome central forme des liaisons covalentes avec tous les atomes périphériques conduit à des difficultés. Ainsi, il faudrait admettre dans le cas de $(PtCl_4)$ l'existence d'une structure $PtCl_4$ (l'état d'hybridation du platine étant dsp^2), correspondant à un ion plan. Dans ce cas, il y aurait capture de deux électrons par l'atome Pt. Or, si la capture du premier électron peut être exo- ou endothermique, celle du 2ème électron est toujours endothermique. Le « poids » de la forme covalente est donc faible. L'hypothèse la plus probable paraît être celle d'une distribution de charges (de localisation). Le diamagnétisme observé concorde avec la superposition des structures suivantes:



(4 structures) (4 structures) (4 structures) (2 structures)

L'image électrostatique avec accumulation des charges positives sur l'ion central, ne s'applique pas non plus aux ions complexes positifs. Ainsi selon cette image le platine dans $(Pt(NH_3)_4)^{\cdot}$ serait doublement ionisé. Or, cette double ionisation exige une énergie de 26,3 eV dont 17,3 eV pour le second électron, tandis que l'ionisation de NH_3 n'est que de 10,8 eV. Donc là aussi il y aura délocalisation, ce qui est en accord avec le fait que les distances Me—N dans de tels ions sont plus proches des distances covalentes que des distances van der Waals. L'image électrostatique est fausse même pour des complexes du type $(Al(H_2O)_6)^{+++}$.

4. – Période 1950-1952.

On sait que la notion de l'énergie de résonance a été développée à la suite de la constatation que pour des molécules comportant des liaisons doubles conjuguées ou des anneaux phényliques, l'énergie de formation de la molécule dépassait la somme des énergies de formation des différentes liaisons. Ceci était mis en relation avec le fait que de telles molécules ne pouvaient pas être représentées graphiquement par une formule unique comportant seulement des liaisons simples, doubles et triples et ne pouvaient être décrites que par une somme de f.o., dont chacune était choisie de manière à décrire une « structure »

(configuration de valences) possible et dont aucune ne correspondait à la configuration de valence réelle. PAULING a donc introduit la notion que ces différentes « structures » formaient un système « résonant » et que l'existence de cette résonance était responsable de l'excès d'énergie constaté. Cette notion de « résonance » et d'énergie de résonance a été soumise par des savants soviétiques à une critique très sévère et ceci sur plusieurs plans — empirique, théorique et philosophique —. Nous allons examiner successivement ces différents aspects de la critique.

4·1. – *Critiques de caractère empirique.*

TATEVSKIJ [34] a fait la remarque suivante: on considère d'habitude, qu'il existe 3 types de liaisons carbone-carbone, les liaisons simples, doubles et triples et on attribue à chacune une certaine énergie de formation et une longueur de liaison. Cette approximation est très grossière et il n'est pas étonnant que la loi d'additivité ne soit pas strictement respectée. Une approximation meilleure consisterait à tenir compte aussi de l'état d'hybridation des atomes de carbone liés par de telles liaisons, ou ce qui revient au même, de leur nombre de coordination. Dans une troisième approximation, on tiendrait compte de la nature chimique des atomes auxquels ces atomes de carbone sont liés par ailleur [35].

Examinons la deuxième approximation. Les atomes de carbone peuvent se trouver dans un état d'hybridation

(*a*) ψ_s, ψ_{Px}, ψ_{Py}, ψ_{Pz} le nombre de coordination correspondant étant de 4 ,

(*b*) ψ_s, ψ_{Px}, ψ_{Py}, ψ_{Pz} le nombre de coordination correspondant étant de 3 ,

(*c*) ψ_s, ψ_{Px}, ψ_{Py}, ψ_{Pz} le nombre de coordination correspondant étant de 2 .

Nous désignerons ces atomes de carbone selon leur nombre de coordination par $C^{(4)}$, $C^{(3)}$, et $C^{(2)}$ et les ordres de liaisons par des traits de valence de la manière habituelle.

Les 9 combinaisons suivantes sont possibles: $C^{(4)}$—$C^{(4)}$, $C^{(4)}$—$C^{(3)}$, $C^{(4)}$—$C^{(2)}$, $C^{(3)}$=$C^{(3)}$, $C^{(3)}$—$C^{(3)}$, $C^{(2)}$ = $C^{(2)}$, $C^{(3)}$—$C^{(2)}$, $C^{(2)}$—$C^{(2)}$, $C^{(3)}$=$C^{(2)}$ (allène). A ces combinaisons, TATEVSKIJ ajoute la liaison C—C dans le benzène, la liaison C—C dans la graphite et la liaison C—C dans les composés polynucléiques. L'expérience montre alors que les longueurs de liaison sont fixes pour chacun de ces 2 types de valence et ne dépendent pas du reste de la molécule (sauf pour les alkyls aromatiques) [34]. De même, si on attribue à chacun de ces types une énergie de liaison calculable à partir des molécules simples, il est possible de représenter les chaleurs de formation de 72 hydrocarbures différents, dont les 12 qui ont servi à établir les énergies de liaison [36]. Les écarts les plus grands s'observent pour le triphenylméthane (12 kcal), le phénantrène (9 kcal), le pérylène et le triphénylbenzène (8 kcal) et les hexaméthylbenzène (6 kcal).

Pour tous les autres corps l'écart est inférieur à 3 kcal. L'énergie de conjugaison disparaît donc dans cette approximation, et l'idée d'énergie de résonance perd toute base expérimentale. Toutefois, comme l'a remarqué BAGDASARIAN [1, p. 382], TATEVSKJI nie non seulement l'existence de l'énergie de résonance, mais aussi la notion de conjugaison, dans ses différentes manifestations. Le butadiène, le styrolène, etc., sont d'après cet auteur des composés « additifs », les liaisons doubles ayant le même caractère que dans l'éthylène (ordre de doubles liaisons $\equiv 1$) les liaisons simples sont les mêmes que dans l'éthane (ordre de doubles liaison $= 0$). Il est toutefois incapable d'aller jusqu'au bout et se voit obligé d'introduire comme types de valence particulière celle du benzène (ordre de double liaison $= \frac{1}{2}$), celle du graphite (o.d.l. $= \frac{1}{3}$) et celle de composés polynucléiques (o.d.l. entre $\frac{1}{2}$ et $\frac{1}{3}$).

Il est évident que les types de liaison introduits plus haut ne suffisent pas pour expliquer les différences entre les chaleurs de formation de différents isomères. TATEVSKIJ [35] introduit donc des sous-types. Dans les alcanes, $C^{(4)}$—$C^{(4)}$, le premier atome de carbone est primaire, mais peut être lié à un atome de carbone primaire, secondaire, tertiaire ou quaternaire, le 2ème atome de carbone peut être secondaire, tertiaire ou quaternaire et ainsi de suite. De même un atome d'hydrogène peut être lié à un atome de carbone primaire, secondaire, etc.. Les énergies de liaison, les volumes molaires, les réfractions moléculaires, etc., varient légèrement d'un des 9 sous-types à un autre et si l'on en tient compte, les énergies de formation et les autres propriétés moléculaires deviennent additives. Ainsi, à l'aide de 9 énergies de liaison (constantes), on peut représenter les chaleurs de formation de 44 paraffines isomères [37]. L'écart avec l'expérience est en général très inférieur à 1 kcal, sauf pour le 2, 2, 4-tryméthylpentane où il atteint 2 kcal.

SOKOLOV [38] a examiné la relation qui existe entre le principe de l'additivité et l'argument souvent énoncé en faveur des approximations L.V. et O.M.; à savoir qu'elles permettent de représenter l'énergie de systèmes conjugués ou de molécules phényliques, à l'aide d'un facteur empirique (α ou β selon la méthode employée) identique à 10% près, pour toutes les molécules et multiplié par des coefficients numériques calculables x_i et N_i (nombre de liaisons ou de cycles). Il a montré que chaque fois que l'énergie du système pouvait être représentée sous la forme

$$E = \sum_{i=1}^{1} x_i N_i \alpha$$

(ce qui est le cas pour les approximations L.V. et O.M.), on pouvait construire un nombre infini de systèmes de coefficients numériques, satisfaisant à certaines conditions, pour lesquels α ne varie pas de plus de 10% au passage d'une molécule à une autre. Dans le cas de calculs par les méthodes L.V. et O.M. ces conditions imposées aux coefficients numériques x_i se trouvent remplies.

Il a attiré aussi l'attention sur une autre objection, soulevé déjà par Mamotenko [39] et que l'on peut faire à la théorie actuelle des effets de conjugaison: actuellement on suppose que ces effects sont dûs dans leur totalité aux électrons π, l'énergie de conjugaison (ou de délocalisation) étant définie comme la différence des énergies de deux liaison π se trouvant, d'une part à grande distance et d'autre parte à proximité l'une de l'autre. Or, rien ne prouve que la contribution des liaisons σ, qui sont perturbées par la proximité des deux liaisons π, soit négligeable. Ces objections n'enlèvent rien à la valeur des résultats *qualitatifs* de la théorie actuelle des effets de conjugaison; celle-ci permet par exemple de comprendre la différence d'interaction entre noyaux phéniliques coplanaires et non coplanaires.

Syrkin [4, page 116] a rassemblé quelques faits expérimentaux qui ne cadrent pas avec la théorie de résonance. Ainsi d'après les données récentes la distance des carbones du groupement $—CH_2—CH_2—$ dans le dibenzyl est raccourcie (1,48 Å), tandis que l'énergie de dissociation en radicaux benzyle est faible (45-48 kcal). Il en est de même, d'après les mesures de Halilov avec le chlorure de geranylamine. L'explication réside probablement dans l'existence d'une hyper-conjugaison. La distance des carbones dans l'hexafluoroéthane (1,44 Å) est inférieure à celle existant dans l'éthane, tandis que d'après la théorie de la mésomérie, on devrait s'attendre à un allongement de la liaison à cause de l'accumulation des charges positives sur les atomes. Il en est de même dans le cas des composés halohydrogénés de l'hydrazine.

Le moment électrique du triphénylméthyle sodium est de 7,2 *D*, tandis que celui de C_2H_5Li n'est que de 0,7 *D*, tandis que les moments des dérivés chlorés, bromé et iodé du triphénylméthyle sont les mêmes que ceux des éthyles correspondants.

Ces résultats ne peuvent pas être expliqués à l'aide de l'ypothèse de la mésomérie et sont probablement en relation avec la grande affinité électronique du triphénilméthyle.

Enfin, d'après les mesures de Kitajgorodskij les liaisons C—C ne sont pas de même longueur ni dans le naphtalène et ses dérivés, ni, ce qui est plus étrange, dans le 1,4-diméthoxybenzène.

4·2. – *Objections théoriques.*

Les premières objections théoriques contre la théorie de résonance, ont été soulevées par Sokolov [40], mais la première discussion serrée du problème est due à Tatevskij [41]. La critique de Tatevskij est dirigée surtout contre *l'interprétation* que donnent certains chercheurs, des chimistes en particulier des calculs effectués par la méthode L.V. et n'est pas dirigée contre la méthode elle-même. Etant donné le retentissement que ce travail a eu en URSS

nous croyons utile de l'exposer plus en détail, quitte à reproduire certains raisonnements connus.

Un des buts de la chimie quantique est le calcul des paramètres physiques des molécules à l'état fondamental. Etant donné qu'une molécule possède une énergie bien définie et invariable dans le temps elle se trouve dans un état stationnaire et le problème se réduit à la solution d'une équation de Schrödinger ne contenant pas le temps.

La solution exacte est donc donnée par une fonction ψ_0 obéissant à l'équation

$$H(x)\psi_0(x) = E_0\psi_0(x)\,, \tag{1}$$

où E_0 ne dépend pas des coordonnées de l'espace x. Cependant, il est impossible de résoudre cette équation pour des molécules compliquées, et de trouver la fonction d'onde exacte ψ_0; on est par conséquent amené à rechercher une solution approximative, ψ^0, dont l'énergie moyenne $\bar{\varepsilon}^0$ est aussi voisine que possible de la valeur exacte E_0, pour des valeurs de x voixines des distances de liaisons. Une méthode d'approximation utilisable dans ce but est la méthods des variations, qui consiste à construire la fonction $\psi^0(x)$ à l'aide de fonctions $\psi_i(x)$ choisies arbitrairement, et de paramètres C_k, initialement indéterminés et qu'il s'agit de calculer. La fonction ψ^0 sera d'une manière générale donnée par

$$\psi^0(x) = f(C_1, C_2, ..., C_o, \psi_1, \psi_2, ..., \psi_m)\,, \tag{2}$$

et, dans le cas particulier de la « variante linéaire de la méthode de variation » (V.L.M.V.), par

$$\psi^0(x) = \sum_{i=1}^{n} C_i\psi_i(x)\,. \tag{3}$$

Il est important de remarquer que ni la fonction ψ^0, ni les fonctions $\psi_i(x)$ ne sont des solutions de l'équation (1) ni même d'une quelconque équation de Schrödinger; on a

$$\frac{1}{\psi^0(x)}\{H(x)\psi^0(x)\} = \varepsilon^0(x) \tag{4}$$

où maintenant ε^0 est, cependant, une fonction des coordonnées.

La valeur moyenne de l'énergie $\bar{\varepsilon}^0$, donnée par

$$\varepsilon^0 = \frac{\int \psi^{0*}(x)H(x)\psi^0(x)\,\mathrm{d}x}{\int \psi^{0*}(x)\psi^0(x)\,\mathrm{d}x} \tag{5}$$

est une fonction des paramètres C_i qui sont choisis de manière à rendre $\bar{\varepsilon}^0$ minimum. Soit C_i^0 de telles valeurs. On a alors

$$\psi^0(x) = \sum_{i=1}^{n} C_i^0 \psi_i(x) \,. \tag{6}$$

On voit que nulle part n'apparaît l'idée de résonance. L'utilisation de la méthode V.L.M.V. n'implique nullement que les fonctions $\psi_i(x)$ décrivent une structure quelconque, ni que $\psi^0(x)$ soit une superposition de telles fonctions; le choix des fonctions $\psi_i(x)$ est arbitraire; quant à la fonction $\psi^0(x)$ nous demandons uniquement qu'elle soit proche de $\psi^0(x)$ au voisinage des distances de liaison, ce qui signifie ici que les différentes propriétés de la molécule que l'on déduit de $\psi^0(x)$ soient proches de celles que l'on déduirait de la fonction exacte $\psi^0(x)$. Par contre, nous ne pouvons pas exiger de $\psi^0(x)$ qu'elle soit aussi voisine de $\psi^0(x)$ pour des grandes distances internucléaires. Seule la fonction exacte $\psi^0(x)$ peut décrire correctement le système pour toutes les distances interatomiques.

Si nous choisissons les fonctions ψ_i de telle sorte que $\psi^0(x)$ soit voisine de $\psi_0(x)$ à des grandes distances interatomiques nous nous imposons une restriction injustifiée dans le choix des $\psi_i(x)$ et nous nous condamnons à un écart plus grand entre ψ_0 et ψ^0 justement au voisinage des distances d'équilibre, où la concordance maximum est souhaitable.

La méthode qui consiste à choisir comme fonctions ψ_i les fonctions des atomes isolés, permet, en principe, de résoudre non pas le problème chimique, mais le problème physique d'un système d'atomes situés à des distances finies mais grandes par rapport aux distances de liaison. Ce problème peut être résolu rigoureusement par la méthode des perturbations, à condition que l'interaction des particules soit faible. Les modifications des fonctions qui apparaissent dans ce cas ne peuvent que s'amplifier si l'on rapproche les atomes les uns des autres à des distances de liaison. L'examen de ces perturbations est utile pour comprendre la signification physique des fonctions utilisés habituellement dans la méthode V.L.M.V.

Deux cas sont à envisager, selon que le système initial est dégénéré ou ne l'est pas. Examinons d'abord le second cas. Soit $\varphi_n^0(x)$ et $E_n(x)$ les fonctions d'ondes et les énergies du système de n particules (atomes p. ex.) quand celles-ci se trouvent à une distance infinie, c'est-à-dire quand l'interaction entre elles est nulle, et soit $W(x)$ l'opérateur déterminant la perturbation. On sait que dans ce cas les fonctions d'onde des différents états du système perturbé seront

$$\varphi_k(x) = \sum_n \left\{ \delta_{nK} C_n^{(0)} + \sum_{n \neq k} \frac{W_{nk}}{E_K^{(0)} - E_n^{(0)}} \cdots + \right\} \varphi_n^{(0)}(x) \,. \tag{7}$$

et leurs énergies

$$E_k = E_K^0 + \int \varphi_K^{(0)*} W \varphi_K^{(0)} \, dx \,. \tag{8}$$

On voit que quoique les fonctions $\varphi_n^{(0)}$ du système non perturbé ne soient pas des fonctions propres du système perturbé, elles constituent dans ce cas des approximations d'ordre zéro pour les f.o. du système perturbé.

Nous allons voir maintenant qu'il n'en est pas de même si le système initial est dégénéré, c'est-à-dire s'il possède au moins deux et en général f_K états décrits par des fonctions $\varphi_{1K}\varphi_{2K} \dots \varphi_{fK}$ et possédant la même énergie $E_K^{(0)}$. C'est le cas par exemple de deux atomes d'hydrogène, composés de deux protons et de deux électrons, chacun des électrons pouvant se trouver lié à l'un ou a l'autre proton. Pour un tel système initial les solutions de l'équation de Schrödinger sont d'une part les fonctions $\varphi_{\alpha K}^0$ elles-mêmes, d'autre part les combinaisons linéaires de ces fonctions

$$\Phi_K^{(0)} = \sum_{\alpha=1}^{f} C_\alpha \varphi_{\alpha n}^0 \tag{9}$$

satisfaisant au principe de Pauli.

Pour le système perturbé, par contre, seules les combinaisons linéaires constituent une approximation d'ordre zéro

$$\Phi_K(x) = \sum_{\alpha=1}^{f} C_{K\alpha} \varphi_{K\alpha}^0(x) \,. \tag{10}$$

Ce sont donc uniquement ces combinaisons linéaires qui décrivent un état du système perturbé, et non plus les f.o. isolées $\varphi_{\alpha K}^{(0)}$ du système non-perturbé. En d'autres termes, dans un système initial dégénéré l'apparition d'une perturbation dûe à l'interaction des particules, aussi faible soit elle, provoque un changement qualitatif discontinu: d'un ensemble de particules isolées, le système se transforme en un tout organique, lié par des forces d'interaction. Si les particules se rapprochent, leurs distances tendent vers les distances d'équilibre, ce changement qualitatif deviendra plus important, mais son sens restera le même.

Examinons à titre d'exemple l'ion H_2^+. A l'état non perturbé le système proton-atome d'hydrogène (proton + électron) est dégénéré et peut être décrit par deux f.o. $\varphi_a^{(0)}$ et $\varphi_b^{(0)}$, selon que l'électron se trouve près du proton a ou près du proton b. Si une interaction apparaît, le système ne pourra plus être décrit, même à l'approximation d'ordre zéro que par une combinaison

$$\Phi_0 = C_1 \varphi_a^{(0)} + C_2 \varphi_b^{(0)} \,. \tag{11}$$

Les valeurs de C_1 et de C_2 peuvent être déterminées, soit par la V.L.M.V., soit par la méthode des perturbations, dans la mesure où cette méthode peut être appliquée à des perturbations aussi importantes. Si l'on utilise donc (11) comme f.o. approchée pour décrire la particule chimique H_2^+, on ne peut attribuer ni à $\varphi_a^{(0)}$ ni à $\varphi_b^{(0)}$ la signification d'une fonction décrivant un état quelconque de cette particule. La situation est identique pour les molecules H_2, C_6H_6 et autres. On ne saurait assez insister sur le fait, qu'aucune des f.o. rentrant dans l'expression pour l'approximation d'ordre zéro de la f.o. du système perturbé n'a un sens physique si elle est prise isolément; elle ne détermine aucun état du système, aucune « structure ». Seule la combinaison linéaire dans sa totalité détermine un état stationnaire du système.

Si dans la V.L.M.V. on utilise les fonctions Φ de l'approximation d'ordre zéro résultant d'un calcul de perturbation, les différentes fonctions individuelles ψ_i, dérivées des f.o. du système non-perturbé, n'ont aucune signification physique. On n'a pas le droit de les considérer comme décrivant des états « superposables » ou « résonants » de la molécule, tout comme on n'a pas le droit de considérer Φ comme résultant d'une superposition ou d'une résonance de structure.

C'est pourtant ce qu'ont fait, parmi beaucoup d'autres Syrkin et Djatkina [1] et Bočvar [5]. Ce dernier considère par exemple que les fonctions $\psi_i(x)$ de l'équation (6) peuvent être choisies de manière à décrire chacune un état stationnaire, correspondant à une « structure » imaginable de la molécule, la superposition de telles structures correspondant à la fonction $\psi^0(x)$, décrivent mieux la molécule que chacune des « structures » prises isolément. En fait de tels schémas de structure purement imaginaires, n'ont rien à voir avec la structure chimique réelle de la molécule. Elles ont un sens tout différent: elles représentent simplement une transcription graphique de toutes les distributions des spins des électrons possibles à priori. Ce caractère formel des formules structurales de la théorie de la résonance en tant que transcription graphique des fonctions de spin, résulte clairement du fait que la théorie de la résonance ne considère que la résonance entre des « structures canoniques » ou irréductibles. Du point de vue chimique il n'y a aucun sens à parler de la dépendance ou de l'indépendance linéaire des différentes formules de structure chimique. Comme l'indique Terenin [4, pp. 32, 33], il est permis de représenter les fonctions de spin du benzène par les figures

Fig. 1.

mais on n'a pas le droit de parler d'une résonance entre les structures

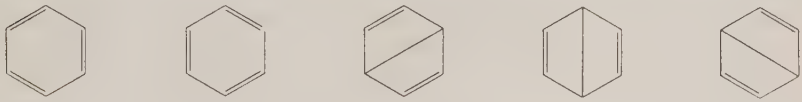


Fig. 2.

qui correspondent à des structures chimiques bien définies.

Il est, évidemment, encore moins permis d'attribuer à la résonance des conséquences physiques, par exemple d'attribuer la plus grande stabilité d'un composé par rapport à un autre, à l'augmentation du nombre de structures résonantes (*). Ou encore d'expliquer qualitativement les propriétés physico-chimiques d'un composé en postulant « l'existence d'une résonance » et en écrivant des « structures » des états résonnants, convenablement choisies, sans faire des calculs par le V.L.M.V.

Les savants soviétiques, sont tous d'accord pour constater qu'il n'existe pas de lien logique univoque entre la V.L.M.V., qui constitue une méthode valable d'approximation, et la théorie de la résonance qui est une interprétation fausse des différents termes d'un développement en série comme correspondant à des « structures » imaginables (voir par exemple Terenin (**) [4, p. 37], Sahporonov [4, p. 184], Syrkin [4, p. 124]).

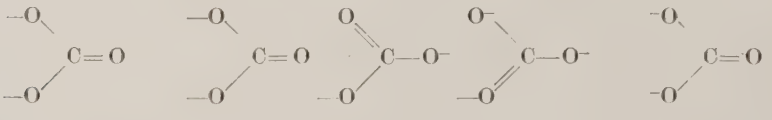
La critique de la théorie de la résonance s'applique aussi à la « mésomérie » d'une liaison entre une liaison purement ionique et une liaison purement covalente. On peut effectivement obtenir, par approximations successives une même f.o. « correcte » ψ_0 en partant de l'une ou de l'autre de ces structures décrites en première approximation par des f.o. φ_i et φ_r respectivement, en ajoutant des termes pour tenir compte de la différence d'électroaffinité des constituants, de la polarisation du nuage électronique, etc.. [Ceci ne signifie pas toutefois que l'on obtiendra une bonne approximation ψ de la fonction ψ_0 en additionnant les f.o. de première approximation, multipliées par des coefficients C_i et C_a choisis à l'aide de la V.L.M.V. Ces coefficients ne permettraient donc pas de déterminer le « degré d'ionicité » d'une liaison. – M. Magat.]

Cette critique de l'usage, que l'on fait souvent des « structures limites » ne signifie évidemment pas que l'on ne puisse pas se servir d'abstractions en

(*) Voir aussi page 433.

(**) Ici, comme ailleurs, en nous référant à Terenin, nous nous référons, en réalité, au rapport d'une Commission, nommée par l'Académie des Sciences de l'URSS, présenté par cet auteur et qui a servi de base à la Discussion [4]. Outre Terenin, cette commission comprenait V. N. Kondratev, I. L. Kunian, V. V. Korsak, M. T. Kabacnik, et N. D. Sokolov.

chimie (Terenin, [4, p. 52]). Il est parfaitement légitime de décrire l'ion CO_3^{--} par (I) en considérant cette formule comme une abstraction, dans le même sens que la notion du « corps solide » dans la mécanique rationnelle. Toutefois pour passer de cette structure abstraite à la structure réelle, il faut non pas écrire trois formules identiques avec une permutation des oxygènes portant la charge négative (II), qui « résonneraient » entre elles, mais indiquer le sens de déplacement des électrons (III), une telle description faisant apparaître le sens des modifications qui doivent être apportées à (I) pour rendre compte de la réalité physique



I. II. III.

Structure « abstraite » Structures « résonnantes » Structure « réelle »

Si l'on adopte la position des chercheurs soviétiques et que l'on rejette la théorie de résonance, il faut se demander à quoi sont dûes les différences entre les structures « abstraites » et les structures « réelles » et comment en tenir compte. Une indication dans ce sens est donnée dans le rapport de Terenin [4, pp. 12-67].

Ce rapport commence par un examen des origines de la notion de la structure chimique, qui sont étroitement liées au nom de Butlerov (voir par exemple Beilstein, *Handbuch der Organischen Chemie* (Leipzig, 1893, p. 5). Tandis que pour Kekulé, les formules chimiques rationnelles n'étaient qu'un moyen commode pour décrire les réactions chimiques d'un corps, mais en aucun cas ne pouvaient exprimer sa structure, c'est-à-dire la position des atomes, pour Butlerov [43, p. 71] la structure chimique est la distribution des forces chimiques des atomes, et comment ces derniers, en agissant, directement ou indirectement les uns sur les autres, se réunissent pour former une particule chimique. « Si nous essayons de déterminer la structure chimique et réussissons à la représenter par nos formules, celles-ci seront des vraies formules rationnelles. Pour chaque corps, une seule formule rationnelle est possible, et quand on connaîtra les lois générales reliant les propriétés chimiques des corps à leur structure chimique, une telle formule exprimera toutes ces propriétés » [44, p. 78]. Du fait que dans CH_2O l'hydrogène et l'oxygène sont liés au carbone, mais ne sont pas directement reliés entre eux, « il ne résulte pas qu'ils n'exercent aucune action les uns sur les autres; seulement, cette interaction sera d'une autre catégorie » [44, p. 452]. Si les atomes existent effectivement... je ne vois pas pourquoi les tentatives pour déterminer leur distribution spatiale seraient vouées à l'échec » [44, p. 86].

Pour comprendre les références continuelles à BUTLEROV (*) dans les articles soviétiques récents consacrés au problème de la structure chimique, il est nécessaire de remarquer que ses conceptions satisfont aux exigences de la dialectique matérialiste qui forme la base philosophique de la science soviétique. Il en résulte une identité: conceptions de BUTLEROV = conceptions de dialectique matérialiste, les deux termes de cette identité pouvant être utilisés indistinctement dans la discussion d'un problème.

La mécanique quantique permet en principe de décrire la liaison chimique et de prévoir la structure et les propriétés des molécules, qui sont déterminées par la distribution de la densité du nuage électronique.

Toutefois, seules les molécules les plus simples peuvent être traitées d'une manière quantitative. Dans le cas des molécules plus compliquées, on est obligé de se contenter d'approximations très grossières (L.V. et O.M.) qui ne peuvent fournir que des renseignements qualitatifs, très précieux néanmoins, car ils permettent, entre autre, de prévoir certains phénomènes.

Le nuage électronique est polarisable, les électrons π des liaisons doubles l'étant plus que les électrons σ. Les déviations du schéma simple sont justement dues à de telles déformations du nuage électronique.

Ces déformations peuvent provenir, soit des atomes participant à la liaison, s'ils sont d'électronégativité ou d'électroaffinité différentes, soit des atomes ne participant pas directement à la liaison. Dans le cas de liaisons σ, ce dernier effet n'influence que les liaisons les plus voisines; on l'appelle effet d'induction.

Dans le cas des électrons π, surtout s'il s'agit de systèmes conjugués qui, grâce à une distribution plus uniforme de la densité électronique, possèdent une énergie, mais aussi une déformabilité plus grandes que les systèmes non conjugués, l'effet inductif n'intervient que d'une manière secondaire.

Le gros de l'action des atomes non liés, qui peut s'exercer sur des liaisons assez éloignées, s'appelle l'effet de conjugaison.

L'effet de conjugaison peut être, soit statique, soit dynamique, c'est-à-dire n'apparaître q'au moment d'une réaction chimique.

L'effet de conjugaison, appelé souvent effet mésomérique ne provient pas d'une « superposition » de structures ou d'une transformation de structures limites « non-perturbées » en structures réelles par perturbation mutuelle, comme le suggère INGOLD, mais d'une polarisation du nuage électronique.

(*) Remarquons que les idées de BUTLEROV étaient bien connues de son temps en Europe occidentale (il a séjourné en Allemagne et en France). Elles ont indubitablement influencé les débuts de la chimie structurale comme en témoigne WURTZ dans son *Traité de Chimie Organique*. Toutefois, par la suite, BUTLEROV est tombé dans l'oubli, même en Russie. C'est la réimpression de ses œuvres [44] qui a remis sa contribution en lumière.

Selon la nature (« accepteur » ou « donneur ») du substituant, les électrons π se déplaceront vers le substituant ou dans la direction opposée.

La représentation de tels effets ne peut pas être faite à l'aide des formules structurales classiques qui ne reflètent que les positions relatives des atomes et les ordres de liaison. Les détails (distribution des électrons π, effet de conjugaison, effet d'induction, etc.) doivent être représentés par adjonction d'autres symboles, indiquant les déplacement observés des électrons tels que des flèches droites ou courbes, les pointillés, des signes + et —.

4·3. – *Objections philosophiques.*

Une dernière série d'objections contre la théorie de la résonance et certaines autres notions utilisées dans la théorie de la liaison chimique, est de nature philosophique et relève de la théorie de la connaissance.

Semenčenko [4, p. 135] [42] et Batuev [45] ont examiné le problème général de la relation entre les différents termes apparaissant au cours d'un traitement mathématique d'un problème physique (ou chimique) et la réalité physique.

Dans quelles conditions les notions résultant d'un tel calcul peuvent-elles être utilisées pour des conclusions générales dans le cadre de la théorie de le connaissance?

D'après Semenčenko ces notions correspondent à une réalité physique, si elles satisfont au critère de l'invariabilité physique ou logique. On comprendra mieux de quoi il s'agit, par un exemple. Supposons que nous avons une notion admise dans une théorie quelconque dont le caractère approximatif est reconnu. Si nous passons maintenant de la théorie approchée à la théorie exacte (ou à une autre théorie approchée du même phénomène), et si la notion conserve entièrement sa signification, nous dirons qu'elle présente l'invariabilité physique et reflète par conséquent la réalité. Ainsi, les notions de masse et de charge d'un électron gardent leur signification dans n'importe quelle théorie électronique, et correspondent donc à une réalité physique.

Il n'est est pas de même de certaines notions de la théorie de la liaison chimique.

Ainsi, pour obtenir une représentation correcte d'un système chimique par la *méthode d'approximation* L.V., on doit tenir compte de *toutes* les interactions électroniques possibles, en introduisant dans l'expression de la f.o. « totale » les fonctions de spin pour tout l'ensemble des « structures canoniques ». Il est évident qu'il y aura une différence entre l'énergie calculée et celle que l'on calcule dans une approximation encore plus grossière en ne tenant compte que d'*une seule* fonction de spin, par exemple dans le cas du benzène de la fonction de spin qui correspond à une structure du type Kekulé. Cette diffé-

rence d'énergie est appelée « énergie de résonance » (*). Il est évident qu'elle ne peut correspondre à aucune réalité physique, car elle représente simplement l'erreur commise en utilisant une méthode d'approximation trop grossière. Ce caractère irréel de l'« énergie de résonance » se confirme si l'on effectue le calcul par la méthode O. M. Dans ce cas, aucun terme n'apparaît dans le calcul, qui puisse être interprété comme l'« énergie de résoannce » (voir aussi TERENIN [4, p. 34]).

L'énergie d'échange est un autre exemple d'une notion fréquemment utilisée, mais ne correspondant pas à une réalité physique.

Voici comment cette notion a été introduite.

Dans leur célèbre travail sur la molécule H_2, HEITLER et LONDON ont considéré comme état initial deux atomes d'hydrogène séparés et ont calculé leur interaction par la méthode des perturbations. Etant donné que les atomes d'hydrogène isolés possèdent une symétrie sphérique, ils se sont servis de coordonnées sphériques. Si l'on conduit le calcul de cette manière il apparaît une intégrale d'origine électrostatique qui n'apparaît pas si l'on n'utilise pas la mécanique quantique, et que les auteurs ont légitimement appelé « intégrale d'échange ». Cette intégrale donne une contribution importante à l'énergie totale du système, contribution qu'il est devenu d'usage d'appeler « énergie d'échange », et on lit couramment que la liaison chimique est due aux « forces d'échange » que l'on oppose aux forces coulombiennes, quoique en réalité les deux soient de nature électrostatique.

Le même problème de la molécule d'hydrogène a été résolu par JAMES et COOLIDGE d'une manière différente. Ces auteurs ont considéré la molécule H_2 comme une entité qualitativement différente de deux atomes d'hydrogène juxtaposés, et ils ont résolu le problème d'un système de deux noyaux et de deux électrons, en utilisant le système de coordonnées adapté à ce problème, à savoir le système de coordonnées elliptiques (comme on le fait depuis longtemps en astronomie pour des problèmes à deux centres). L'énergie et la distance internucléaires calculées par ce procédé sont en meilleur accord avec l'expérience que celles calculeés par la méthode de Heitler et London. On peut donc considérer la méthode de James et Coolidge comme plus exacte que la méthode des perturbations. Or, si l'on utilise ce procédé, il n'apparaît dans le calcul aucun terme identifiable avec l'« énergie d'échange ». Les notions de l'« énergie d'échange » et de « forces d'échange » ne sont donc pas liées au phénomène de la liaison chimique, mais uniquement à une méthode de calcul. Plus encore: dans la méthode de perturbations, la valeur de l'« énergie

(*) [Dans cette conception l'« énergie de résonance » serait d'autant plus grande que le nombre de structures canoniques sera plus élevé parce que l'erreur commise, en ne tenant compte que d'une seule de ces structures canoniques, sera relativement plus importante. – M. MAGAT.]

d'échange » dépend du système initial adopté. Elle n'est pas la même, par exemple, si l'on prend comme système initial deux atomes d'hydrogène ou un ion H_2^+ et un électron.

On peut donc conclure que les « forces d'échange » ne représentent pas une réalité physique, ou, si elles le font, c'est sous une forme très imparfaite.

Faute de place, il nous est impossible d'exposer ici d'autres arguments de nature diverse, dont il a été fait état au cours de la Discussions [4], ainsi que dans divers articles que nous nous contenterons de citer [45-52].

5. – Période 1952-1953.

Il résulte de la discussion dont nous avons donné les points essentiels une nécessité de repenser les bases de la théorie de la liaison chimique et de rechercher de nouvelles voies d'approche.

C'est à cet examen qu'est consacré un important travail de Semenčenko [42] dont nous avons déjà donné quelques extraits. Il nous paraît utile de les compléter.

Semenčenko rappelle que dans l'équation de Schrödinger, qui sert de point de départ de la chimie quantique, on suppose que la vitesse de la lumière est infinie. Il en résulte que cette équation ne peut pas décrire les interactions magnétiques, et qu'elle est donc mal adaptée pour la description de la liaison chimique où le spin joue un rôle primordial. Il serait plus correct de partir de l'équation de Dirac. Malheureusement jusqu'à très récemment on ne savait même pas écrire l'équation de Dirac pour un système de plusieurs particules, et si maintenant, grâce au travail de Širokov [53], il est devenu possible de le faire, la solution ne peut pas encore être donnée. On a été et on est encore réduit à utiliser les solutions des équations de Schrödinger et de les multiplier par les fonctions de spins qui tiennent compte des propriétés magnétiques des électrons.

C'est en se servant de telles solutions que Heitler et London ont réussi les premiers, à résoudre d'une manière approchée le problème de la molécule H_2. Nous avons déjà vu la critique à laquelle Semenčenko soumet ce travail, tout en reconnaissant son importance.

Nous ne rappellerons ici qu'un seul point de cette critique, celui qui concerne le choix de l'état initial: il était en effet constitué par l'ensemble de deux atomes d'hydrogène séparés. Il paraît plus logique de partir de la molécule déjà formée, comme l'ont fait ensuite James et Coolidge.

Des succès importants ont été obtenus par la suite à l'aide des méthodes d'approximation L.V. et O.M. Il faut néanmoins remarquer qu'au cours des 25 années de son existence, la mécanique quantique n'a pu élaborer des méthodes pour résoudre exactement l'équation de Schrödinger sauf pour l'atome H

et les atomes de ce type, c'est-à-dire à un électron de valence. La solution exacte des systèmes multiélectroniques n'a pas encore été trouvée et on cherche toujours à réduire un problème multiélectronique à un problème monoélectronique. C'est pour cette raison que les f.o. monoélectroniques possèdent une telle importance dans la mécanique quantique appliquée à la chimie. Cette réduction au problème monoélectronique est certainement justifiée dans le cas d'atomes, mais il est douteux qu'elle le soit dans le cas de molécules, puisque la liaison est justement assurée par deux électrons. C'est là que réside le point faible des méthodes L.V. et O.M. qui construisent la f.o. des molécules à partir des f.o. monoélectroniques des atomes.

Le problème fondamental de la chimie quantique n'est pas le calcul précis des constantes moléculaires, mais l'établissement et l'interprétation théorique de différents types de liaisons moléculaires et de structures moléculaires possibles. Ce but n'est pas atteint et la chimie quantique a plutôt embrouillé la question (*).

Voici comment d'après SEMENČENKO on devrait formuler le problème. Une molecule est un système de n noyaux de charges $Z_1, \ldots, Z_n$ et de $\sum_{i=1}^{n} Z_i$ électrons. Le problème quantique peut être écrit sous la forme de l'équation de Schrödinger:

$$(12) \qquad \frac{1}{2}\sum \Delta_i \psi + \left\{ E - \sum_i \sum_j \frac{Z_i Z_j}{R_{ij}} + \frac{1}{2}\sum_i \sum_K \frac{Z_i}{r_{iK}} - \sum_k \sum_{mm} \frac{1}{r_{km}} \right\} \psi = 0 ,$$

où R_{ij} = la distance internucléaire, r_{km} celle des électrons entre eux, r_{iK} celle entre les électrons et les noyaux; ψ est une fonction des coordonnées de tous les noyaux et électrons. Si les positions des noyaux sont fixées, l'équation (12) détermine une énergie E_0 de l'état stable de la molécule et la fonction propre ψ_0 (ψ_{0i} s'il y a dégénérescence), dont la distribution spatiale donne des renseignements sur la structure de la molécule et le caractère de la liaison. Malheureusement, on ne peut espérer résoudre cette équation et on est obligé de recourir à des approximations, tout comme on le fait dans le cas des atomes (méthode de Fock-Hartree par exemple). Mais ce serait faux d'utiliser pour les molécules les mêmes approximations que pour les atomes. Il faut se laisser guider, pour le choix des approximations, par la nature du système de particules envisagé. Les molécules sont constituées de noyaux, d'électrons les entourant et,

(*) Sur ce point particulier, SEMENČENKO se trouve en accord avec SLATER [54] qui écrit: « The writer feels that the understanding of chemical problems according to the quantum theory has been set back, rather than advanced, by the great desire which many scientists have had to derive numerical results on the basis of inadequate approximations and unjustified use of simplified theories ».

ce qui est essentiel, par des *paires d'électrons* de liaison. Il faudrait donc utiliser, non pas les fonctions monoélectroniques du type hydrogène comme dans le cas des atomes, mais des fonctions d'onde biélectroniques. Fock a montré en effet [55] qu'il était possible de construire une fonction d'onde totale possédant les caractéristiques de symétrie nécessaires pour décrire l'état total d'une molécule, en se servant de fonctions d'onde biélectroniques pour les électrons couplés et de fonctions d'onde monoélectroniques pour les électrons célibataires. Il a également indiqué une méthode pour construire la fonction totale, de symétrie donnée, en tenant compte de tous les électrons présents. Malheureusement, on n'a encore jamais essayé d'utiliser cette méthode. La difficulté réside dans l'absence de fonctions électroniques. Il y aurait la possibilité de résoudre rigoureusement le problème de la molécule H_2 et de se servir, avec précaution évidemment, de la fonction électronique ainsi obtenue pour attaquer des problèmes plus complexes. [La poursuite des travaux de Mohrenstein, auxquels Freud [56] vient de faire une contribution, et du travail de Coolidge et James s'impose dans ce but. – M. Magat.] Semenčenko suggère aussi une autre possibilité d'attaquer le problème, à savoir de tenter le développement pour les molécules, d'un modèle vectoriel dans le genre de celui que Fock avait développé pour les atomes.

Ces suggestions de Semenčenko qui a tracé un programme pour un avenir lointain, n'ont pas encore été appliquées. Quelques tentatives ont néanmoins été faites pour traiter les molécules comme des entités plutôt que comme des produits d'addition d'atomes. Certaines sont assez grossièrement empiriques, d'autres cherchent à appliquer les méthodes qui ont été utilisées pour les métaux, en traitant la totalité ou une partie des électrons comme un gaz électronique.

Ainsi Sarkisov [57] a indiqué une formule semi-empirique pour calculer les distances interatomiques dans les molécules organiques. L'auteur avait trouvé que pour les métaux où des électrons de valence sont délocalisés, la distance interatomique est une function relativement simple du nombre atomique et du nombre d'électrons de valence.

Dans le cas de molécules organiques où les électrons sont localisés, les calculs sont plus complexes, car il faut tenir compte de la répulsion entre les électrons participant à des liaisons et les électrons des atomes 1 et 2 n'y participant pas, ainsi que de la répulsion des électrons de valence entre eux. Sarkisov évalue la répulsion à l'aide de la formule pour l'énergie d'un gaz électronique. Il aboutit, pour la longueur de la liaison, à l'expression suivante:

$$r_0 = C' \frac{F_1^{1/3} + F_2^{1/3} + F_f^{1/3}}{(f_1 + f_2)^{1/3}}, \tag{13}$$

où f_1 et f_2 sont les nombres d'électrons des atomes participant aux liaisons,

F_1 et $F_2 \approx (Z - f_{max})$ et $F_f = (f_1 + f_2)^{2/3}$. L'accord avec l'expérience est remarquablement bon pour un très grand nombre de composés contenant des atomes très divers.

BAGDASARIAN [59] a essayé de traiter les hydrocarbures aromatiques par la méthode du gaz électronique (G.E.). Voici son raisonnement: H. KUHN [et NIKITINE. – M. MAGAT] ont utilisé récemment avec succès l'image quasi-métallique pour calculer à l'aide d'équations de mécanique ondulatoire, les niveaux énergétiques des molécules aromatiques. D'autre part, FRENKEL [60] avaix montré que l'on pouvait calculer les propriétés des métaux en se servant de la méthode du gaz électronique de Fermi. Ce gaz électronique, composé des électrons de valence, se trouve dans un champ des « restes » atomiques chargés. L'énergie totale H du gaz dégénéré se compose de l'énergie (cinétique) au 0° absolu, proportionnelle à puissance 5/3 de la densité électronique (δ) et de l'énergie potentielle U des interactions des électrons entre eux et avec les restes atomiques. Si on admet que dans les composés aromatiques toutes les liaisons sont équivalentes, $\delta = n/l$, où n est le nombre des électrons π, l le nombre de liaisons σ. On en déduit:

$$H = \boldsymbol{k} l \left(\frac{n}{l}\right)^{5/3} + U, \tag{14}$$

où $\boldsymbol{k}$ est un coefficient de proportionnalité.

Pour déterminer l'effet énergétique de conjugaison ε, il faut comparer H à H_0, l'énergie d'une « molécule étalon », dans laquelle les électrons π forment des liaisons biélectroniques ($n = 2$, $l = 1$). On trouve

$$H_0 = \boldsymbol{k} \frac{n}{2} (2)^{5/3} + U_0, \tag{15}$$

et

$$\varepsilon = H - H_0. \tag{16}$$

Si l'on suppose que la différence $U - U_0$ est négligeable par rapport à la différence d'énergie cinétique lorsqu'on passe d'une molécule à une autre, on peut facilement calculer ε en unités relatives et le comparer aux valeurs expérimentales. BAGDASARIAN a comparé pour 22 hydrocarbures les valeurs de ε_{exp} à celles que l'on calcule par la méthode G.E., L.V. et O.M. Les écarts entre les ε_{calc} par les trois méthodes sont faibles. Toutefois, la méthode G.E. ne donne pas des valeurs différentes pour les différents isomères, comme le fait la méthode O.M.. Il est possible que ce défaut soit lié au fait d'avoir négligé dans les calculs les différences des énergies potentielles.

Le reproche que l'on peut adresser aux travaux de Bagdasarian et de Sarkisov, c'est que ces auteurs appliquent tous les deux des formules statistiques valables pour un grand nombre d'électrons, à un ensemble d'électrons très réduit.

Volkenštejn et Borovinskij ont calculé les spectres électroniques des composés aromatiques [61] et l'anisotropie de la susceptibilité magnétique du benzène, du naphtalène et de l'anthracène [62] par la méthode de la « boîte de potentiel », en supposant dans le cas du benzène que les six électrons π peuvent se déplacer librement sur la périmètre de l'hexagone, qu'on remplace d'ailleurs par un cercle de rayon équivalent. Le calcul n'est évidemment plus compliqué pour le naphtalène et l'anthracène. On obtient ainsi « une caisse » (ou un « puits ») de potentiel, unidimensionnelle et fermée, ce qui simplifie beaucoup la solution des équations de Schrödinger. Si l'accord numérique avec les données expérimentales laisse à désirer, le tableau d'ensemble des propriétés ainsi calculées correspond bien aux observations.

Medvedev [63] considère que les liaisons monoélectroniques sont beaucoup plus répandues dans la nature qu'on ne l'a supposé jusqu'à présent et montre comment l'existence éventuelle de telles liaisons permettrait de représenter facilement les formules structurales pour un gran nombre de composés organiques et minéraux dont il est difficile de donner une représentation dans le cadre des liaison biélectroniques.

Nous n'avons pas signalé dans cette revue les nombreux travaux soviétiques sur la liaison hydrogène. Il nous semble néanmoins utile de signaler celui de Sokolov [64, 65] parce qu'il peut avoir une portée plus générale. Sokolov étudie à l'aide de la mécanique quantique l'interaction entre un groupement polaire A—H (dont —OH, —NH, FH sont des exemples) et un atome B. La difficulté de la théorie électrostatique de la liaison H réside dans le fait que la distance entre H et B est beaucoup plus petite que la somme des rayons van der Waals de H et de B. Ceci ne peut s'expliquer par l'attraction électrostatique seule, trop faible pour compenser l'énergie de répulsion. Sokolov montre que deux effets additionnels doivent être pris en considération: d'une part à la suite de l'électroaffinité de A la densité des électrons autour de H dans la direction opposée à *A* est fortement diminuée, ce qui réduit la répulsion entre H et B de quelques 20 à 40%. D'autre part, une attraction apparait, due à la modification de la densité électronique de B dans le champ des A-H. Des considerations de ce genre peuvent être importantes aussi pour d'autres cas de formation de complexes moléculaires.

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Sur les travaux de magnétisme en U.R.S.S.

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(ricevuto il 22 Ottobre 1953)

SOMMAIRE

1. Ferromagnétisme. 1. Aimantation spontanée. 2. La théorie de la courbe technique d'aimantation. **2. Diamagnétisme et paramagnétisme. – 3. Bibliographie.**

On m'a demandé de donner pour le *Nuovo Cimento* un aperçu des travaux sur le magnétisme publiés en URSS. Ma connaissance de la langue russe m'a sans doute valu cet honneur, mais j'ai beaucoup hésité avant d'entreprendre le travail sur un sujet aussi vaste et qui, par ailleurs, dépasse mon domaine. J'ai accepté, pensant faire œuvre utile, même si le travail devait présenter des lacunes et des erreurs. Je me suis inspiré de PAUL LANGEVIN qui a tellement contribué à la compréhension des phénomènes magnétiques et qui a dit une fois: «le travail scientifique procède comme tout travail humain, il ne peut être poursuivi qu'en gardant le contact avec toutes les ressources de la collectivité humaine».

La difficulté d'obtenir régulièrement les publications scientifiques russes et à laquelle s'ajoute l'absence quasi-totale de tout contact personnel font qu'on a des difficultés supplémentaires pour se renseigner sur les travaux effectués en URSS.

Je n'aurais certes pas entrepris ce travail, qui devait se faire en un temps très court, si je n'avais pas pu m'assurer de la collaboration de Monsieur ISRAEL EPELBOIN et sans l'aide de qui ce travail n'aurait pas pu être mené à bien.

Dans l'esprit de démentir un peu le dicton qui veut que «les absents ont toujours tort», nous avons pris comme règle d'exposer le point de vue russe pour les priorités scientifiques; ceci ne veut pas dire que nous avons pu re-

chercher la justification de cette attribution. Nous avons surtout insisté sur la question du ferromagnétisme, chapitre où le développement semble être plus important et que nous avons traité en premier lieu.

Nous n'avons pas eu le temps d'assimiler l'énorme quantité de travaux parus en URSS, ce qui expliquera que certains auteurs ont été cités par préférence à d'autres et que certains sujets n'on peut-être pas été appréciés à leur juste valeur; nous nous excusons donc devant les auteurs qui peuvent se sentir lésés.

1. – Ferromagnétisme.

La première contribution russe à l'étude du ferromagnétisme daterait de 1871. Il s'agit des recherches expérimentales de A. G. Stoletov [1] sur les courbes d'aimantation relevées au balistique sur des échantillons ferromagnétiques toroïdaux fermés permettant de connaître la perméabilité magnétique non influencée par la forme du corps ferromagnétique. Cette méthode est généralement utilisée. Les travaux de B. L. Rozing (1892) [2] sur la théorie du ferromagnétisme par contre n'ont qu'un intérêt historique.

On sait que la théorie du champ moléculaire de P. Weiss admet une aimantation spontanée indépendante du champ magnétique externe et qui s'annule au-delà d'une certaine température (point de Curie). Comme la théorie de l'aimantation spontanée, faisant intervenir une orientation parallèle des spins d'electrons, permet d'expliquer les phénomènes fondamentaux du ferromagnétisme, nous grouperons dans le premier chapitre les travaux russes sur l'aimantation spontanée et son influence sur certaines propriétés non magnétiques des substances ferromagnétiques (propriétés thermiques, électriques, « galvanomagnétiques », thermoélectriques, etc.).

La deuxième hypothèse de la théorie de Weiss suppose que les corps ferromagnétiques contiennent des domaines où l'aimantation spontanée est homogène, même avant l'établissement d'un champ magnétique extérieur qui tend à imposer ensuite une orientation commune à l'ensemble: l'étude de ces domaines élémentaires se confond en une certaine mesure avec celle de la courbe technique d'aimantation et elle permet d'expliquer dans une large mesure le comportement des substances ferromagnétiques sous l'action d'un champ magnétique. Les publications russes sur ce sujet sont groupées dans le deuxième chapitre.

Enfin, nous avons également inclus les travaux russes sur le comportement des ferromagnétiques dans les champs variables et l'ensemble des travaux sur la variation des propriétés magnétiques en fonction du temps (viscosité magnétique) ainsi que les travaux traitant les phénomènes gyromagnétiques. La fabrication des matériaux ferromagnétiques sort du cadre de cet exposé, mais cer-

taines publications citées signalent de remarquables performances de matériaux magnétiques (métaux et céramiques). Il semble donc que les équipes spécialisées dans les questions de fabrication collaborent étroitement avec les grands centres de recherches scientifiques du ferromagnétisme. Ces centres sont disséminés à travers toute l'URSS et sont animés par plusieurs savants bien connus pour leur travaux sur le ferromagnétisme, notamment ARKAD'EV e KONDORSKIJ à l'Université de Moscou, POLIVANOV à l'Institut d'Energétique de Moscou, DORFMAN à l'Institut Hydrométéorologique de Leningrad, AKULOV à l'Université de Minsk, JANUS à l'Université de l'Oural, VONSOVSKIJ à Sverdlovsk, KERENSKIJ à Krasnojarsk, etc..

L'étude du ferromagnétisme semble intéresser de nombreux chercheurs soviétiques, car il existe plusieurs ouvrages d'ensemble (indiqués en chiffres romains au début de la bibliographie); les deux colloques soviétiques sur le magnétisme qui ont eu lieu à Sverdlovsk en 1946 et en 1951 ont été en grande partie consacrés à l'étude des phénomènes ferromagnétiques (les rapports présentés à ces colloques ont été publiés dans *Izv. Akad. Nauk SSSR Ser. Fiz.*, **11** (1947); **12** (1948) et **16** (1952). Enfin, les indications bibliographiques qui accompagnent les publications russes et les traductions en russe des travaux de SNOEK, KITTEL, etc., semblent indiquer que les chercheurs suivent de très près les travaux sur le ferromagnétisme publiés dans les autres pays.

1·1. – *Aimantation spontanée.*

Parmi les anciens travaux soviétiques sur la nature de l'aimantation spontanée, on cite souvent dans la littérature russe ceux de DORFMAN qui a étudié le passage d'un faisceau d'électrons bien canalisé à travers des feuilles minces de nickel [3] et son travail qui signale une anomalie de la conductibilité thermique du nickel [4]. Celle-ci se traduit, au point de Curie, par un changement caractéristique de l'aimantation spontanée. A la même époque (1928) FRENKEL [5] a émis l'idée que le ferromagnétisme est une forme particulière de paramagnétisme dû au spin électronique et il a été, avec HEISENBERG, à l'origine de la théorie de l'aimantation spontanée basée sur l'énergie d'échange et sur le principe d'exclusion de Pauli. Parmi les publications russes relativement anciennes sur la théorie quantique de la variation de l'aimantation spontanée avec la température, citons celles de AHIEZER [6], LANDAU et LIFŠIC [7]. Ceux-ci ont donné une théorie thermodynamique des changements de phase [8-9] applicable au ferromagnétisme.

Signalons également le travail de KANER [10] qui a développé une théorie statistique du ferromagnétisme en utilisant une méthode de moments analogue à celle de la théorie des alliages ordonnés. Actuellement, la théorie quantique du ferromagnétisme est étudiée en URSS principalement par VONSOVSKIJ et son école; le lecteur pourra se reporter à l'ouvrage très détaillé [IV] écrit

en collaboration avec Šur ainsi qu'aux deux rapports présentés aux colloques du magnétisme de Sverdlovsk [11].

Parmi les résultats obtenus par cette école, citons un modèle de ferromagnétisme à plusieurs électrons tenant compte notamment de l'interaction entre les électrons des couches *s* et *d* [11]. Ce modèle a été appliqué en particulier à l'étude de la variation, en fonction de la température, de l'aimantation spontanée dans le cas des métaux et dans celui des alliages [11]; pour les alliages seulement, voir aussi [12-14].

La notion de l'ordre magnétique à courte distance a été utilisée déjà en 1939 [15] pour expliquer la persistance de l'anomalie de la conductibilité thermique au-delà du point de Curie. Vonsovskij a développé cette notion en donnant des bases théoriques à la différence entre les points de Curie *W* ferro- et paramagnétique [IV].

L'apparition de l'aimantation spontanée au point de Curie se traduit par des variations anormales de nombreuses propriétés non magnétiques. L'école de Sverdlovsk a utilisé la théorie quantiques des métaux pour expliquer certaines de ces anomalies, comme celles de la variation de la résistivité électrique avec le carré de l'aimantation [11, 16-19] et pour établir des formules relatives aux phénomènes galvanométriques, thermoélectriques et thermomagnétiques [19-21]. Au sujet des travaux de cette école, citons également une étude sur l'effet photoélectrique dans les ferromagnétiques [22] et des mesures de l'effet Hall entre 77 et 1 053 °K dans le fer électrolytique [23]. Ces mesures confirment la variation linéaire de la constante de Hall en fonction du carré de l'aimantation spontanée; ces résultats avaient d'ailleurs été précédemment trouvés pour le nickel par Kikoin [24]. On trouve dans les publications précitées des résultats qui prouvent que la différence de potentiel de l'effet Hall n'est pas proportionnelle au champ magnétique, mais à l'aimantation. L'effet Hall dans les alliages à surstructure du type Ni_3Mn a fait l'objet des publications de Komar et Volkenštejn [25]. Ces travaux, effectués à Sverdlovsk, confirment la variation linéaire de la constante de Hall avec le carré de l'aimantation spontanée. Signalons qu'une théorie quantique de l'effet Hall a été établie par Samojlovič à l'Université de Czernovicz [26] où se poursuivent également des travaux sur l'anomalie d'autres propriétés non magnétiques des ferromagnétiques au point de Curie [27].

On sait que l'apparition de l'aimantation spontanée s'accompagne toujours d'une déformation anisotrope (magnétostriction) due au changement d'équilibre dans le réseau cristallin. Cette magnétostriction entraîne des anomalies des propriétés mécaniques des ferromagnétiques mais comme elles ne sont mises en évidence que si l'échantillon est soumis à un champ magnétique extérieur, nous grouperons la bibliographie sur l'ensemble de ces phénomènes dans le chapitre consacré à la courbe technique de l'aimantation.

Au sujet des anomalies thermiques, rappelons que l'aimantation spontanée

est à l'origine de la variation réversible de la température au cours de l'aimantation adiabatique (effet magnétocalorique prévu en 1905 par LANGEVIN et découvert en 1919 par P. WEISS). Les expériences sur des monocristaux de Ni ont montré que cet effet dépend de l'énergie libre dûe à l'anisotropie magnétocristalline [28] en accord avec la théorie d'AKULOV de l'anisotropie magnétique [II].

Cette dernière théorie a permis de montrer que les formules obtenues pour le calcul de la magnétostriction dans les champs magnétiques forts, où prédomine le phénomène de rotation de l'aimantation, peuvent être appliquées au calcul de n'importe quel effet pair (c'est-à-dire ne dépendant pas des signes du champ ou de l'aimantation). C'est le cas, notamment des phénomènes galvanomagnétiques, thermoélectriques, thermomagnétiques, galvanoélectriques, etc., et c'est pour contrôler cette théorie que de très nombreux travaux expérimentaux ont été publiés sur ce sujet [29-43].

Dans le domaine de l'antiferromagnétisme, citons les travaux expérimentaux concernant l'effet magnétocalorique [44] et l'anomalie de la conductibilité thermique [45] et également les essais de théorie de l'antiferromagnétisme [47-48] qui présentent de nombreuses lacunes. Le rapport de DORFMAN [49] au colloque de magnétisme de Sverdlovsk semble montrer que son laboratoire s'intéresse également à l'étude du ferromagnétisme et l'antiferromagnétisme des semiconducteurs. On trouve également un rapport sur les ferromagnétiques non métalliques du type ferrite présenté par G. A. SMOLENSKIJ [50] de l'Institut de Chimie des Silicates, qui interprète en particulier le comportement des ferrites doubles de zinc et de nickel en les considérant comme des antiferromagnétiques imparfaits, en accord avec la théorie du ferromagnétisme de L. NEEL (1948). Sur l'étude de la magnétite, voir [51, 52] et sur celle des ferrites, voir [53-55].

1·2. – *La théorie de la courbe technique d'aimantation.*

Les bases actuelles de la théorie de la courbe technique d'aimantation remontent aux travaux de N. AKULOV [57] sur l'anisotropie magnétique et la magnétostriction, qui ont permis d'aborder l'interprétation du comportement d'un ferromagnétique soumis à un champ magnétique extérieur. (Les résultats d'AKULOV et de son école sont exposés dans son ouvrage d'ensemble [II]). Il a montré que la courbe technique d'aimantation ne peut être liée aux forces d'échange qui déterminent uniquement l'aimantation spontanée, mais à l'interaction magnétique entre le moment des spins des électrons et de leur orbite. Dans ses premiers travaux AKULOV a étudié de façon purement classique les interactions magnétiques dans les cristaux ferromagnétiques. Depuis ses idées ont été reprises et développées à l'aide de la mécanique quantique dans d'autres pays et en URSS [II].

Dans les champs forts on sait que l'allure de la courbe technique d'aimantation est essentiellement déterminée par la rotation de l'aimantation spontanée et les constantes de magnétostriction à saturation peuvent se calculer suivant les principales directions cristallographiques, d'après la loi d'anisotropie magnétique d'Akulov. Cette loi indique en effet que la valeur de ces constantes varie linéairement en sens inverse de la température absolue, ce qui a été confirmé par K. P. Belov et O. N. Agasjan [58, 59]; cependant, les résultats trouvés par d'autres auteurs étrangers ou russes [60] révèlent, en fonction de la température, des variations plus compliquées qui se rapprochent de celles prévues par la théorie des quanta [IV]. Signalons que dans le cas du nickel A. Ja. Vlasov [61] a vérifié récemment cette variation linéaire de la magnétostriction à saturation en fonction de la température en effectuant des mesures dans les champs magnétiques suffisamment élevés, entre - 196 °C et 300 °C. Au sujet de la variation de la magnétostriction à saturation en fonction de l'aimantation spontanée dans le cas du fer, voir le travail de Titov [62].

On sait que dans les champs faibles la courbe technique d'aimantation est déterminée surtout par des déplacements, reversibles ou non des parois des domaines élémentaires; ce qui entraîne des difficultés dans l'étude de la magnétostriction. Akulov [57] a fait des calculs basés sur la statistique des domaines de l'aimantation spontanée et il a repris cette méthode plus tard en collaboration avec Kondorskij [63], en tenant compte de l'influence des tensions internes (voi aussi [64]). Il a également expliqué l'effet ΔE, c'est-à-dire la diminution du module d'Young par suite de l'aimantation [II]. La méthode statistique a été utilisée par Vladimirskij [65] pour le calcul des courbes de magnétostriction des polycristaux. Les constantes de magnétostriction varient de façon très compliquée avec la constitution d'alliages, mais il est important de déterminer leurs variations pour étudier les substances dont les spins sont orientés suivant certaines directions privilégiées (texture magnétique [66]). Il existe aussi une magnétostriction qui entraîne une variation de forme au cours de l'aimantation; la théorie de ce phénomène a été élaborée par Simonenko [67]. Pour d'autres formes de magnétostriction, voir [68-70]. Les propriétés magnétoélastiques des alliages ferromagnétiques ont été étudiées dans les champs forts par Belov [71] à l'Université de Moscou. Il a signalé la variation de la magnétostriction en fonction de la traction élastique effectuée sur des alliages Fe 64% Ni 30% et Fe 44% Pt 56% et a pu expliquer [71] l'anomalie du coefficient de dilatation thermique des alliages du type invar.

Depuis les premiers travaux d'Akulov on sait que l'anisotropie magnétocristalline joue un rôle essentiel dans le mécanisme de l'aimantation. Il est particulièrement important de connaître sa variation en fonction de la température. En URSS cette question a été étudié surtout par Kirenskij qui, déjà en 1937 [72], a montré que la constante d'anisotropie magnétocristal-

line du fer variait davantage avec la température que celle de l'aimantation à saturation (voir aussi [73]). Pour le nickel voir [74] et pour les alliages voir entre autres [75-77].

Kirenskij [78] a remarqué une hysteresis thermique de l'anisotropie magnétique propre aux alliages ferromagnétiques irreversibles (par exemple pour les ferronickels contenant moins de 30% de nickel); la réalisation d'un dispositif très sensible pour la mesure de la magnétostriction par compensation de la dilatation thermique a permis de découvrir également une hysteresis thermique de la magnétostriction dans le cas du nickel [79].

Puzej [80] de l'Institut Central de Recherches Scientifiques de la Métallurgie, a étudié de façon très complète, en fonction de la vitesse de refroidissement, les constantes magnétocristallines et de magnétostriction de monocristaux sphériques d'alliages Fe-Ni, Fe-Ni-Cr, Fe-Ni-Mo, ayant une teneur nickel comprise entre 44% et 99,4%; parmi eux, citons notamment des permalloy susceptibles de présenter une surstructure du type $FeNi_3$ et une perméabilité très élevée correspondant à de très faibles valeurs des constantes d'anisotropie magnétique et de magnétostriction. Un autre travail expérimental récemment effectué à l'Université de Moscou donne avec détails [81] la variation de la courbe technique d'aimantation de ces alliages en fonction de l'état d'ordre. Au sujet du permalloy voir aussi [82, 83].

Depuis 1930, Frenkel et Dorfman [84] ont établi des formules reliant les dimensions des domaines à celles de l'échantillon ferromagnétique et ce travail a encore été cité récemment dans la littérature au cours de discussions sur l'origine du champ coercitif des aimants en poudre finement divisée. La théorie du champ coercitif est étudiée depuis plusieurs années par E. Kondorskij qui a publié dernièrement un exposé d'ensemble de ses travaux [85]. Une théorie des domaines élémentaires a été proposée par Landau et Lifšic [86, 87], en tenant compte de l'énergie de l'anisotropie magnétique. Leur calcul a été généralisé par Sirobokov [87] qui a tenu compte du champ magnétique externe (voir aussi [88, IV]).

On sait que l'effet Barkhausen constitue une preuve directe de l'existence des domaines élémentaires. Signalons à ce sujet un récent travail de l'Institut de Krasnojarsk sur l'influence de la température sur les sauts irreversibles de l'aimantation des fils de nickel [89]. Une autre preuve de l'existence des domaines est donnée par les figures de Bitter, que Akulov a utilisés depuis 1932 et dont l'emploi s'est généralisé depuis. Voir [91-93]. Au sujet de ce dernier travail signalons que Eremin, de l'Institut Central de Technologie et de Construction de Machines, a appliqué cette méthode pour étudier les défauts des matériaux ainsi que la structure des aciers et de divers alliages [93-bis].

La théorie de la courbe technique d'aimantation dans les champs forts et celle de la rotation de l'aimantation à saturation sont basées sur les formules d'Akulov [57] et [II] qui sont utilisées universellement et l'on peut ainsi cal-

culer la courbe d'aimantation des monocristaux et des polycristaux. Cependant des difficultés persistent par suite de l'impossibilité de tenir rigoureusement compte de l'interaction magnétique entre les différents cristaux. De nombreux dispositifs ont été réalisés pour effectuer des mesures dans ce domaine. Signalons à ce sujet le magnétomètre tournant réalisé par AKULOV en collaboration avec BRJUHATOV qui a été utilisé en Russie pour les travaux expérimentaux de nombreux chercheurs (voir par exemple [94-97]).

AKULOV et KIRENSKIJ [98] ont effectué des calculs de la courbe d'aimantation en faisant certaines hypothèses sur la répartition des tensions. Ceci permet de déterminer les constantes de magnétostriction et d'anisotropie magnétique. Des travaux analogues ont été effectués par JANŠIN [99]. Dans le but de déterminer les courbes d'aimantation du nickel lorsque son énergie magnétocristalline est faible GRABOVSKIJ [100] lui a fait subir des tensions mécaniques à basse température. Signalons que l'influence des tensions sur les caractéristiques d'aimantation a été étudiée à l'Université de Gorkij [101-103] et dans d'autres centres de recherches (voir par exemple [104-107]).

La « loi d'approche de l'aimantation vers la saturation » proposée par AKULOV en 1931 n'est valable que pour une structure homogène. Ceci a été confirmé par des mesures effectuées à l'Université de Moscou, au champ de 600 à 3 000 Oe, sur des alliages du type FeMo et FeVa [108], qui montrent que les matériaux hétérogènes se comportent conformément à la théorie de Néel (1948). Au sujet de la loi d'approche de l'aimantation vers la saturation voir également [109]. En vue d'étudier la susceptibilité reversible dans le domaine des champs forts on a récemment réalisé à l'Université de l'Oural un électro-aimant [110] qui a permis de vérifier pour les champs de 12 000 Oe la loi d'approche de l'aimantation vers la saturation dans le cas de nombreux alliages doux et durs [111].

En considérant l'aimantation comme un phénomène de rotation pure, AKULOV et ses collaborateurs [112] ont également calculé les pertes par hystérésis dans les champs tournants. Au sujets des pertes par hystérésis et de l'origine du champ coercitif dûs à des phénomènes de rotation et à l'inversion de l'aimantation, voir [113, 114]. BRJUHATOV [115] a montré expérimentalement que la valeur du champ coercitif ne peut être expliquée par un simple effet de rotation irreversible. KONDORSKIJ a montré que le cycle d'hystérésis et le champ coercitif sont déterminés également par l'arrêt de la croissance des germes d'aimantation [116].

La théorie des courbes d'aimantation dans les champs faibles et moyens a été développée en URSS par KONDORSKIJ principalement [111], [116]. Ces théories ont été vérifiées expérimentalement [117, 118]. En s'appuyant sur ses calculs il a été possible d'établir des relations entre la perméabilité magnétique et les tensions élastiques externes [119], qui ont été vérifiées récemment [120] à l'aide de la méthode magnétométrique [121], la magnéto-

striction étant relevée à l'aide d'un dispositif à levier optique [122]. Ces derniers travaux ont été effectués à l'Institut de Physique du Métal de l'Oural où l'on poursuit des travaux systématiques sur les traitements thermomécaniques et thermomagnétiques, c'est-à-dire sur la variation des propriétés magnétiques dûes à l'application de tension ou de champ magnétique au cours des traitements thermiques [123-129]. L'emploi d'un nouveau traitement thermomagnétique [130] a permis à M. V. Dehtjar, de l'Université de Moscou, d'obtenir des ferronickels à cycle d'hystérésis rectangulaire. Signalons que le traitement thermomagnétique est utilisé également pour l'obtention des aimants permanents [131] et notamment du magnico, dont la structure a été étudiée récemment au microscope électronique [132, 133].

La question de la variation de la perméabilité initiale avec la température et notamment l'effet Hopkinson ont été étudiés par de nombreux auteurs russes [127, 134, 135]. D'autre part, comme l'a montré Dehtjar [136], la perméabilité initiale dépend de nombreux facteurs, en particulier de la désaimantation. Sur l'influence du mode de désaimantation voir un travail récent [137] et également [138, 139]. Enfin au sujet des pertes par hystérésis voir [140, 141].

On est gêné pour établir la théorie des courbes techniques d'aimantation par la variation des propriétés magnétiques en fonction du temps (traînage ou viscosité magnétique). A ce sujet citons le travail de A. Mitkevič [143] qui a montré que le phénomène de trainage ne peut être expliqué par les courants de Foucault. De nombreuses publications ont paru sur la viscosité magnétique; principalement celles d'Arkad'ev et son école qui ont apporté une large contribution en étudiant surtout le comportement des substances ferromagnétiques dans les champs alternatifs. C'est pour tenir compte du trainage magnétique que Arkad'ev a introduit dès 1913 la notion de perméabilité complexe dans les équations de Maxwell et il a été le premier à donner l'allure correcte de la variation de la perméabilité en fonction de la fréquence. Ses travaux sont exposés en détail dans [I] et [II] et dans des publications plus récentes [144, 145] ainsi que dans celles de ses élèves; P. V. Telesnin et ses collaborateurs poursuivent actuellement l'étude de la viscosité magnétique [146-148]. Ce dernier phénomène est étudié également à l'Université de l'Oural [149-152]

Le comportement des phénomènes dans les champs alternatifs est étudié par Polivanov et son école [II] [153, 154], qui, entre autres, a expliqué les anomalies de la variation de la perméabilité en haute fréquence en tenant compte de la structure réelle des ferromagnétiques. Cette question est étudiée également par Kirko à l'Université de Riga [155]. Signalons encore des récentes publications d'Akulov sur une théorie des anomalies des pertes par courants de Foucault [158].

D'autre part, en partant de la théorie de la courbe technique d'aimantation

Landau et Lifsič [86] ont mis en évidence dès 1935 la possibilité d'une résonance ferromagnétique du cristal soumis à un champ magnétique alternatif, de direction perpendiculaire à celle de l'axe de facile aimantation. Cette résonance a été trouvée expérimentalement à Kazan en 1944 par Zavojskij [157]. Ses expériences permettent de déterminer le facteur de Landé g qui doit être égal à 2 pour le spin de l'électron. De nombreuses expériences se poursuivent dans plusieurs pays; en URSS voir [158-161]. Les résultats donnent des valeurs de g supérieures à 2 et aucune explication satisfaisante n'en a encore été trouvée.

2. – Diamagnétisme et paramagnétisme.

Dans les chapitres précédents nous avons donné un aperçu sur les travaux concernant le ferromagnétisme; nous insisterons un peu moins sur la question des dia- et paramagnétisme. L'apport russe dans ce domaine est, comme on le sait, considérable. Des physiciens comme P. Kapica, Dorfman, Frenkel, Landau, Šur, Tamm, etc., sont bien connus. Un travail d'ensemble sur le magnétisme est donné par Vonsovskij [IV]. Nous reproduisons la bibliographie de cet auteur.

Comme l'a fait ressortir E. Bauer lors du Congrès de Strasbourg sur le magnétisme [162] les travaux de Mademoiselle Leeuwen avaient montré que la théorie de Langevin était incompatible avec la théorie classique. A la même conclusion arrive Terleckij [163] en montrant que le magnétisme d'un ensemble dans l'état stationnaire était inexplicable dans la théorie statistique classique rigoureusement appliquée.

Le rôle prépondérant des conceptions quantiques est bien établi actuellement. Un fait remarquable a été signalé par Landau en 1930 [164]. D'après le calcul de cet auteur un ensemble d'électrons libres en mouvement se comporterait comme un diamagnétique en présence d'un champ magnétique appliqué perpendiculairement à la direction du mouvement du fait de la quantification des orbites décrites par les électrons en progression. Citons également les beaux travaux expérimentaux de Janus et Šur.

Dès 1922 Einstein et Ehrenfest avaient prévu une émission électromagnétique dans le domaine des ondes hertziennes comme suite du réarrangement de l'orientation des moments magnétiques dans l'édifice atomique et nucléaire sous l'action du champ magnétique. Inspiré sans doute de cette remarque de Einstein et Ehrenfest, Dorfman [165] avait prévu « un effet photomagnétique » consistant dans un changement de l'état magnétique d'un corps para ou ferromagné ique soumis à l'action d'un champ de fréquence radio. Dorfman est ainsi devenu un précurseur dans le domaine qui a permis les célèbres expérieces de Rabi.

L'absorption par résonance sélective a été trouvée en 1944 par ZAVOJSKIJ à Kazan [166]. KOSIREV a donné récemment une conférence à Paris sur la résonance paramagnétique où il a insisté particulièrement sur l'apport russe. Nous nous permettons d'utiliser sa bibliographie en ce qui concerne les auteurs russes. Un article de KOSIREV sur la résonance paramagnétique paraîtra très prochainement dans le *Journal de Chimie-Physique* et nous renvoyons le lecteur à cet article qui traite du problème de la résonance paramagnétique dont l'étude est en progression constante.

Nous ajoutons quelques références sur le magnétisme à très basse température et le magnétisme nucléaire, sujets qui seront sans doute traités par ailleurs.

Une expérience intéressante a été proposée par DORFMAN en 1947 [167] pour mesurer les moments nucléaires. Deux échantillons paramagnétiques liés rigidement et de même nature sont disposés symétriquement entre les pièces polaires d'un électro-aimant dans la région où il existe un fort gradient. Les forces exercées étant égales et de signe opposé le système comportant les deux échantillons reste en équilibre. Si l'un des échantillons est soumis à l'action d'un champ alternatif faible de fréquence élevée perpendiculaire au champ donné par l'électro-aimant, il y aura précession des moments nucléaires provoquant une dissymétrie qui aura son maximum pour une fréquence de résonance avec la précession de LARMOR des spins nucléaires. La mesure de la force exercée à la résoannce sur l'un des échantillons devrait permettre de déterminer à la fois le moment magnétique nucléaire et la valeur du spin formant en quelque façon un pendant nucléaire de l'expérience Einstein-de Haas.

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Nous donnons ici d'autres références de travaux sur le magnétisme en URSS.

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Recent Research on Superconductivity in the U.S.S.R.

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CONTENTS

1. Introduction. – 2. The Intermediate State. – 3. The Effects of Pressure on the Superconducting Transition and Related Topics. – 4. New Superconducting Compounds. – 5. Thin Superconducting Films. – 6. Measurements at Radio Frequencies. – 7. Miscellaneous Experiments. 1. The Superconducting Transition. 2. Thermodynamic Properties. 3. Penetration depth Measurements. – **8. Theoretical Work. – 9. Bibliography.**

1. – Introduction.

Two laboratories — the Institute for Physical Problems of the Academy of Sciences of the USSR (Moscow) and the Ukrainian Physico-Technical Institute (Harkov) — have been active in experimental work on superconductivity. A good deal of this work has been on quite new aspects which had not previously been studied elsewhere, and has opened up new fields of research, while some has been more pedestrian in character, following up or repeating investigations started outside the USSR On the theoretical side, there have also been important contributions, mainly from LANDAU and his school (at the Institute for Physical Problems), and also from GINZBURG (at the Physical Institute of the Academy of Sciences of the USSR (Moscow)). Until about 1946 most of the Soviet researches were published in English or German as well as Russian, and in this review such earlier work will be dealt with only briefly, and attention concentrated on more recent work which has been published only in Russian.

The main experimental contributions have been concerned with (*a*) the

intermediate state, (*b*) the effects of pressure on the transition and related topics, (*c*) new superconducting compounds, (*d*) the properties of very thin films, (*e*) the R.F. properties of superconductors, (*f*) miscellaneous problems including some experiments on the superconducting transition, measurement of penetration depth, and various thermodynamic properties. Most of (*a*) to (*e*) represent pioneer investigations, while (*f*) are mostly of the « follow-up » variety or are of less interest for other reasons. On the theoretical side, the main contribution apart from Landau's theory of the intermediate state, which will be referred to in connection with the experiments of (*a*), is LANDAU and GINZBURG's new phenomenological theory of superconductivity, and some other ideas which affect the interpretation of R.F. experiments. These various apects will now be described separately.

2. – The Intermediate State.

If a superconductor is placed in an originally uniform magnetic field the field remains uniform only if the superconductor has a zero demagnetizing coefficient. If the demagnetizing coefficient ($4\pi n$) is not zero, the lines of force are distorted in such a way as to be tangential to the surface of the superconductor, and the field is no longer the same at all points of the surface. Thus if the applied field H_e is increased, the local field will reach the critical value H_c for destruction of superconductivity at some points of the surface earlier than others (the field at the equator of the ellipsoid is $H_e/(1 - n)$ and is zero at the poles). In these circumstances, destruction of superconductivity is spread over a range of fields, and it has been shown [1, 2] that lines of force pass through the specimen while it is in this so-called intermediate state, with B, the induction, increasing linearly from zero to H_c, as the applied field H_e increases from $H_c/(1 - n)$ to H_c. F. LONDON [2] suggested that in this intermediate state the specimen splits up into some sort of mixture of pure superconducting and pure normal regions, and that the flux flows entirely through the normal regions. The detailed structure of the mixture was first discussed by LANDAU [3], who supposed that the regions are thin laminae which curve slightly as they come to the surface; the curvature is determined by the condition that the field should be just H_c at the surface of the normal laminae. The free energy of such an arrangement is increased by the curvature of the lines of force, and is least for a large number of laminae, but increasing the number of laminae increases the free energy associated with the surface tension at a phase boundary, and the actual laminar thicknesses are determined by the minimization of the total free energy, taking both these effects into account. Later, however, LANDAU [4] realised that his proposed structure was open to the objection that if the field was just H_c at a phase boundary, it would

be less than H_c away from the convex boundary of a superconducting region, and that therefore the normal regions close to the surface of the specimen could reduce their free energy further by becoming partly superconducting. He proposed a new structure in which the normal regions branch in a complicated way, becoming thinner as they approach the surface, until eventually the division into normal and superconducting phases becomes so fine that it is not possible to distinguish the phases. At the surface, then, he supposed that there is a kind of « mixed state », from which the lines of force emerge uniformly out of the specimen, even though in the interior of the specimen the lines of force are constrained to flow only through the normal laminae. As in the earlier calculation, the scale of the structure is determined by the ratio (Δ/d) where Δ is a length characteristic of the surface tension α, defined by $\Delta = 8\pi\alpha/H_c^2$ and d is the characteristic dimension of the specimen (e.g. the thickness of a plate normal to the field). LANDAU showed that although the intervention of the mixed state should make it impossible to reveal the internal structure by studying the distribution of the emerging flux, it ought, nevertheless, to be possible to reveal the structure by examining the flux distribution in a very narrow gap within a specimen, for instance, a gap between two hemispheres. In fact, if the gap is sufficiently narrow, the laminar structure should continue right up to the gap surface from both sides, and the branching which leads to the mixed state should not occur near the gap surfaces unless the gap width exceeds a certain critical value.

With these considerations in mind, ŠAL'NIKOV [5] took up the question of the structure of the intermediate state experimentally, and studied the field distribution over the surface of a narrow gap between two tin hemispheres situated in a field normal to the plane of the gap; his method was to insert a long bismuth wire in the gap and use its resistance as a measure of the transverse field. The relation between resistance and field is non-linear, and therefore the resistance for a given *average* field should be higher if the field had a structure (for instance, that corresponding to H_c over the ends of normal laminae, and zero over the ends of superconducting laminae) than if it were uniform. He found that the resistance was in fact higher than the value to be expected if the average field (B) was uniform, provided the gap was not too wide. This seemed to confirm LANDAU's prediction of a critical gap width, but it turned out later that the true interpretation of the influence of gap width was simply that the bismuth wire was always placed in the centre of the gap, and therefore for wider gaps the discrete structure of the field distribution became smeared out, owing to the lines of force coming together at increasing distance from the surface. In other words, the absence of structure for larger gap width did not really prove that there was no structure close to the gap surface.

In order to get a more objective picture of the structure, MEŠKOVSKIJ and

Šal'nikov [6] developed an ingenious micro-probe method in which a bismuth wire was again used, but now of a length so small as to be comparable with or less than the scale of the expected structure, so that the resistance provided a measure of the actual field at a point rather than an average. The results showed that a fine structure of the field was indeed present, and the following features were found:

1) The structure is more complicated than suggested by a laminar model, showing that any calculable theoretical model is bound to be at best an idealization.

2) The size of the superconducting domains, though somewhat indefinite, is of order 0.2 mm for a tin sphere of radius 2 cm at 3 °K and for $H_e/H_c = 0.8$. This indicates, according to either of Landau's theories, that $\Delta \sim 10^{-5}$ to 10^{-4} cm.

3) The structure is rather different according as the point (H_e, T) in the intermediate state is reached by increasing H_e at constant T or reducing T at constant H_e.

4) The structure close to a gap surface persists even for very wide gaps (i.e. there is no « critical gap width »).

Once this last point was clear, it was evident that Landau's prediction of a uniform mixed state at the surface was not fulfilled, and there was therefore no reason why the internal structure of the intermediate state should not be revealed at the outside surface of a specimen. This was confirmed in further experiments by Meškovskij and Šal'nikov [7] who found structures similar to those in the gap also immediately outside the surface of a tin sphere in the intermediate state. In a later paper Meškovskij [8] studied the detailed topography of normal and superconducting regions over the whole surface of a gap between two hemispheres (rather than merely along one line, as in the earlier investigations).

Following this work, Lifšic and Šarvin [9] have reconsidered the theory and shown that it is only for infinitely large specimens that the Landau branching model should apply. For specimens of a few cm size, the free energy of Landau's earlier non-branching model becomes lower than that of the branching model. They show, in fact, that the lowest free energy is obtained for such specimens if the laminae branch only once or twice and then come out to the surface without further branching (the number of branches increases with size). Their calculations thus explain why the uniform mixed state does not occur in practice. More recently, Šarvin and Balašova [10] have made some new experiments to investigate point 3) above (which suggests that the observed patterns do not represent true thermodynamic equilibrium, such as is envisaged in all the theoretical calculations). Because, presumably, of the difficulty of the micro-probe technique, they reverted to the simpler, but less instructive, method of the long bismuth wire in a gap between two hemispheres.

With this method they could detect no dependence of the results on the order of variation of H_c and T. This is perhaps not surprising, since the method measures only an average characteristic and could hardly be expected to distinguish the detailed differences of structure revealed by the micro-probe method.

The micro-probe method represents an important new advance in technique, but the results obtained so far, although important, do not do more than give qualitative indications of the structure of the intermediate state. Although the method could be used to get much more quantitative information as regards the value of Δ, and the influence of such factors as specimen size and quality, impurity content and temperature, there is no evidence to suggest that the experiments are being continued.

3. – The Effects of Pressure on the Superconducting Transition and Related Topics.

The effect of pressure on the transition temperature T_c, and critical field H_c is of interest, both in as far as it provides material relevant for a theory of superconductivity and in as far as it is thermodynamically connected with the changes of volume, thermal expansion and compressibility in the superconducting transition. The order of magnitude of the pressure effect had been established by Sizoo, de Haas and Onnes [11] in 1925, but no reliable quantitative data existed until the experiments of Lazarev and his collaborators in 1944. Lazarev and Kan [12] developed an ingenious ice-bomb technique in which the high pressure is developed by freezing water round the specimen in a beryllium bronze vessel. The pressure, which was usually of order 1750 atmospheres, was determined from the small changes of dimensions of the bomb, and the change of T_c was found [13] to be about -0.1 °K for this pressure. A more thorough investigation on both tin and indium was later made by Kan, Lazarev and Sudovcov [14], in the course of which it was established that the change of T_c was proportional to p, and changes of H_c were also measured; some rough measurements on lead were also made. More recently Kan, Sudovcov and Lazarev [15] have reported briefly some results on thallium which shows a positive instead of a negative coefficient $\partial T_c/\partial p$ and on mercury, while Alekseevskij [16, 17] and Alekseevskij and Brandt [18] have reported both positive and negative coefficients for different intermetallic superconducting compounds. All the results are summarized in Table I.

The order of magnitude of $\partial T_c/\partial p$ is much larger than would be expected if the change of T_c was associated in any simple way with the change of lattice size caused by pressure. In fact, if l is a lattice dimension $(l/T_c)\ (\partial T_c/\partial l)$

comes out to be of order 30, showing that T_c is exceedingly sensitive to the exact lattice dimensions. It can be shown from thermodynamics that the

TABLE I.

(a) *Values of* $10^{11} \times \partial T_c/\partial p$ (°K dyne^{-1} cm^2)

Tl [15]	In [14]	Sn [14]	Hg [15]	Ta [15]	Pb [14]
~ 1.2	-4.7	-5.8	< 0	< 0	< -3
Bi_3Ni [16]	Bi_4Rh [16]	$BiAu_2$ [18]	Bi_2K [18]	BiLi [18]	Bi_2Pd [17]
0.6	~ 0.3	-3	5.1	~ -6	< 0

(b) *Values of* $10^9 \times \partial H_c/\partial p$ (gauss dyne^{-1} cm^2)

for T (°K) =	3.7	3.3	3.0	2.5	2.15
In [14]	—	7.5	7.1	6.4	6.0
Sn [14]	8.8	7.7	7.4	6.3	—

Note that $\partial^2 H_c/\partial p\, \partial T \to 0$ as $T \to 0$; this is in accord with the prediction of Nernst's theorem.

change of volume in the superconducting transition is given by

$$\frac{V_n - V_s}{V_s} = \frac{H_c}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)_T. \tag{1}$$

This volume change should be very small ($\sim 10^{-7}$) according to the results of Table I, but LAZAREV and SUDOVCOV [19] have succeeded not only in detecting it, but in checking the truth of equation (1) with fair accuracy, by an ingenious method in which the very small changes of volume of tin were revealed by the movements of a bimetallic strip of tin and brass. This experiment is valuable in providing confirmation not only of equation (1) but of the reliability of the quantitative data regarding $\partial H_c/\partial p$. Since 1949 no further experiments in this field have been reported, though the technique of [19] might be used also for studying thermal expansion, and looking for the discontinuity in it predicted by differentiating equation (1) with respect to temperature.

HOTKEVIČ and GOLIK [20] have also investigated the effect of the plastic deformation caused by applying pressures of up to 20000 atmospheres at low temperatures. For tin, indium and thallium T_c was increased by a few tenths of a degree, but no increase was found for mercury. Earlier, LAZAREV and GALKIN [21] had found even greater increases of T_c in tin for the more com-

plicated plastic deformation caused by cooling a tin specimen glued to glass at room temperature (owing to the differential thermal expansion).

4. – New Superconducting Compounds.

In a series of short notes ALEKSEEVSKIJ and collaborators have reported the discovery of superconductivity in a number of intermetallic compounds of bismuth with other metals. A detailed review of the results (except for the most recent ones) has been given by ALEKSEEVSKIJ, BRANDT and KOSTINA [22] and a summary is shown in Table II. These results, although adding to the data which any detailed theory of superconductivity must explain, do not at present find any direct interpretation, except that bismuth must itself

TABLE II. – *Superconducting compounds of bismuth.*

Compound	T_c (°K)	Literature and values of dH_c/dT (gauss/°K) at $T = T_c$	
Bi_2Au	1.7	[23, 24, 25]	100
Bi_3Ba	6	[26]	
Bi_3Ca	1.7, 2.0	[27, 28]	
BiCs	4.75	[29]	160
Bi_2K	3.6	[30, 31]	160, 130
BiLi	2.5	[28] (cf. [32])	
BiNa	2.2	[33, 31]	100, 180
BiNi	4.2	[28]	
Bi_3Ni	3.6, 4.1	[34, 28]	
Bi_2Pd	1.7	[28]	
BiPd	3.7	[17]	
$BiPd_2$	4.0	[17]	
BiRb	4.25	[29]	150
BiRh	2.1	[28]	
Bi_2Rh	2.75, 2.9	[27, 28]	
Bi_4Rh	2.2, 3.4	[27, 28]	
Bi_3Sr	5.5	[26]	

in some sense be « nearly » a superconductor. This view has been confirmed by HILSCH's recent discovery [35] of superconductivity in thin films of bismuth evaporated on to glass cooled to liquid helium temperatures.

5. – Thin Superconducting Films.

The behaviour of thin superconducting films is of considerable interest for the phenomenological theory of superconductivity. Measurements of resistance in a longitudinal magnetic field give information about the size depen-

dence of critical field, about which theoretical predictions have been made, and exploratory measurements of this kind were first made about 15 years ago by Appleyard, Bristow, London and Misener [36] on mercury films, and Šal′nikov [37] on tin films. Such measurements, however, give information of only limited value, since the resistance may remain zero even though part of the film is in the normal state. Much more information can be obtained from measurements of the magnetic moments of films, but such measurements are more difficult to make than resistance measurements, and until recently the only measurements of this kind were those of Alekseevskij [38] who deduced the magnetic moment from the couple acting on the film when the field was not quite parallel to the plane of the film. Alekseevskij's results, however, were far from complete, both because he could not (for technical reasons) cover the theoretically interesting range of temperatures close to T_c, and because there would seem to be certain difficulties of interpretation owing to the possibility of penetration by the normal component of the field. Recently, Lock [39] has also made magnetic moment measurements by another method, but using films which were probably more irregular in structure than those prepared and measured in high vacuum conditions.

Stimulated by the new phenomenological theory of Ginzburg and Landau (see below), Zavaritckij has again taken up this problem experimentally using the technique developed by Šal′nikov, and has made resistance measurements on tin and thallium films, and has also briefly reported some magnetic moment measurements. The resistance measurements on tin [40] are very much more thorough than the exploratory ones of Šal′nikov; the films used were either deposited at 95 °K and annealed at room temperature, or deposited at room temperature, and the sharp transitions (better than 0.01 °K) and the closeness of the transition temperature to that of bulk tin (within about 0.1 °K) gave confidence that the high observed critical fields could be attributed entirely to the small thickness rather than to any peculiarity of structure. The critical field h was measured as a function of d the film thickness over a range from $4.4\cdot10^{-6}$ cm to $1.05\cdot10^{-4}$ cm, and of $T_c - T$ over a range from less than 0.01 °K to 1.3 °K. The values of h, which appear to be about 30% lower than those of Šal′nikov and Alekseevskij, are fitted fairly well by the expressions

$$\frac{h}{H_c} = \frac{\alpha}{d(T_c - T)^{1/2}} \qquad \text{for} \quad (T_c - T)^{1/2} < \beta/d\,, \tag{2}$$

$$\frac{h}{H_c} = 1 + \frac{\gamma}{d(T_c - T)^{1/2}} \qquad \text{for} \quad (T_c - T)^{1/2} > \beta/d\,. \tag{3}$$

In the range where (3) is valid, marked hysteresis in the resistance-field curves appears, which is absent closer to the transition temperature where (2) is valid.

These expressions and the hysteresis behaviour are predicted by Ginzburg and Landau's theory (and also, as we shall see, by the older Casimir-Gorter theory combined with the idea of long range order) where the parameters α, β and γ are defined (*) by

$$\alpha = 2\sqrt{6}a\,, \qquad \beta = \alpha - \gamma = 3.9a\,, \qquad \gamma = a\,, \tag{4}$$

and a is related to the penetration depth λ by

$$\lambda = a/(T_c - T)^{1/2}\,. \tag{5}$$

The values of a deduced from the empirical values of α, β and γ according to (4) come out respectively as 6 ± 0.5, 6.5 ± 0.6 and $8 \pm 1.1 \cdot 10^{-6}$ cm. These should be compared with the values obtained by more direct methods of $(5 \pm 0.5 \cdot 10^{-6}$ cm (Laurmann and Shoenberg [41]), and $4.6 \cdot 10^{-6}$ (Šarvin [42] see below). It appears then that these experiments, though confirming the qualitative predictions of the theory, do not confirm it quantitatively; the same conclusion follows, as we shall see below, from Ginzburg's detailed analysis of the results of Appleyard, Bristow, London and Misener for mercury films.

In a later note, Zavarickij [43] reports measurements on both tin and thallium films, which confirm Šal'nikov's earlier result that films deposited at low temperatures (e.g. 2 °K) behave quite differently from those which have been either deposited at room temperatures, or annealed subsequently to deposition at a low temperature. The principal differences are that the unannealed films have higher transition temperatures, and much higher critical fields, and that though (2) holds, (3) is no longer true. Some results on magnetic moment measurements are also briefly reported; these show that the magnetization curve is much more spread out for an unannealed film than for an annealed one, and continues to tail off to much higher fields. Unfortunately, very few detailed results are quoted, and such interesting questions as the correlation of the magnetization curves and the resistance curves are not mentioned. A detailed analysis of some of these data has been given by Abrikosov [44] on the basis of an extension of Ginzburg and Landau's theory, but it will be convenient to discuss this interpretation later.

Some other aspects of the properties of unannealed tin and thallium films are discussed in another note [45], where it is reported that the transition

(*) Except that the theory predicts the hysteresis change should set in for $\beta = \sqrt{5}a$; Zavarickij appears to find the same value of β from the interaction of (2) and (3) and from the appearance of hysteresis.

temperature, which is about 4.5 °K for fairly thick films (from 10^{-4} cm to 10^{-6} cm), decreases for films thinner than about 10^{-6} cm to about 2.2 °K for $1.1 \cdot 10^{-7}$ cm. For still thinner films, the resistance no longer vanishes, but instead *rises* with decreasing temperature, the rise being most sharp for the thinnest films. Similar results were found for thallium, which could only be made superconducting if thicker than $4 \cdot 10^{-7}$ cm (minimum transition temperatures 2.3 °K, of 2.9 °K for films thicker than 10^{-6} cm and 2.38 °K for bulk thallium). It may be noted that somewhat similar experiments have been made by Buckel and Hilsch [46], who have not, however, found such a marked variation of transition temperature (they do not find the rise of resistance at low temperatures for very thin films either, but their thinnest films were not as thin as those of Zavarickij). These discrepancies make it probable that the properties of unannealed films are very sensitive to the exact experimental conditions. Finally, we may mention that Zavarickij [47] has confirmed Hilsch's discovery of superconductivity in unannealed bismuth films [35] and has found some correlation between the change in optical properties of such films on annealing and the disappearance of their superconductive behaviour.

6. – Measurements at Radio Frequencies.

Hajkin [48] has measured the resistance of superconducting tin at 9 400 MHz as a function of temperature, and obtained results similar to those of Pippard [49] and Fairbank [50] (*). Some results at 18 000 MHz which appear, however, to be only qualitative, have also been reported by Lazarev and Galkin [51] (in this region of frequency qualitative results are of little interest).

More recently Hajkin [52] has also studied the R.F. behaviour of thin tin films (3.8 to $11.9 \cdot 10^{-6}$ cm) at 9 400 MHz. He gives curves of both the resistance R and the change ΔX of reactance (i.e. $X_s - X_n$), which he finds to be positive, rather than, as for bulk tin, negative as functions of temperature, and interprets them in accordance with a calculation by Abrikosov [53], which is based on Landau's suggestion that a superconductor has a very high dielectric constant (see below). Since for thin films it can be shown that in the normal state X_n is much less than R, the positive values of ΔX, which are comparable to R can be taken as equal to those of X_s itself. It will be convenient to defer discussion of Hajkin's results until the relevant theory has been described. Hajkin also refers to some calorimetric measurements of

(*) Hajkin used a resonator with a machined tin surface and this is probably responsible for the low values of σ/l he finds (cf. [50]).

resistance at 27 500 MHz by GALKIN and BEZUGLYJ [54] but this paper has not yet become available.

7. – Miscellaneous Experiments.

7·1. – *The Superconducting Transition.*

LAZAREV, GALKIN and HOTKEVIČ [55] have carried out experiments in which D.C. and A.C. currents were superimposed in a superconducting wire and superconductivity partly or wholly destroyed by suitable combinations of current strengths; the measured quantity was usually the D.C. resistance of the wire. It is easily shown that if the frequency is low enough and if i and i' denote the D.C. current and the amplitude of the A.C. current respectively, the observed D.C. potential V should be zero for $(i'+i)<i_c$, where i_c is the critical current for destruction of superconductivity, and should then reach a maximum for $(i'-i)=i_c$ and finally for further increase of i', should decrease asymptotically to the value Ri, where R is the ordinary D.C. resistance in the normal state. This behaviour was indeed found at 50 Hz, but at sufficiently high frequencies the maximum value of V became less than its calculated low frequency value, and eventually at about $2\cdot10^7$ Hz the maximum no longer occured at all. From these results it was concluded that any possible relaxation time in the superconducting transition must be less than $2\cdot10^{-8}$ s. This conclusion certainly seems justified, but the detailed interpretation of the behaviour of V as a function of i, i', frequency and temperature must be complicated by the skin effect (which is not discussed by the authors) and by the possibility of temperature oscillations in the specimen, if it has not adequate thermal contact with the bath. A proper quantitative discussion of these complications would be very difficult to carry through, and even if it were done, it is unlikely that the experiment would lead to any results of fundamental significance, except for the upper limit of a possible relaxation time. More recently, similar experiments have been carried out elsewhere [56] and there has been some disagreement about the details of the results and their interpretation [57, 58].

Other experiments which bear on the kinetics of moving phase boundaries in the superconducting transition have been carried out both by the Harkov group [59, 60, 61, 62] and by ALEKSEEVSKIJ [63, 64]; here again the conditions of the experiments were not such as to lend themselves to a clear cut quantitative interpretation, and so they will not be further discussed. It is convenient to mention here a theoretical study by LIFŠIC [65] of the effects of eddy currents in limiting the movement of a boundary between normal and superconducting phases. This discussion is parallel to one by PIPPARD [66]

and we shall only mention here that it is in good agreement with experiments by FABER [67], in which the experimental conditions were deliberately chosen to make a quantitative interpretation possible.

7·2. – *Thermodynamic Properties.*

SAMOJLOV [68] has measured the critical field curve of cadmium and found substantial agreement with previous measurements. He has also measured the specific heat [69] down to about 0.3 °K in both normal and superconducting states, and shown that in the superconducting state the variation is as T^3 (as with most other superconductors), and that the variation of the specific heat difference agreed with that predicted thermodynamically from the critical field data. The specific heat measurements involve some ingenious technical refinements, and are the first ones reported on metals below 1 °K. LAZAREV and HOTKEVIČ [70] have measured the critical field curve of tantalum, and shown that (as with other « hard » superconductors), the critical fields may be drastically reduced by annealing at a high temperature in high vacuum.

7·3. – *Penetration Depth Measurements.*

ŠAL'NIKOV and ŠARVIN [71] developed a new method of measuring the penetration depth λ on macroscopic specimens (already measured by several other methods elsewhere). This method consisted essentially in oscillating the temperature of a specimen at about 4 Hz and observing the small changes of flux due to the corresponding oscillations of λ, from which values of $\mathrm{d}\lambda/\mathrm{d}T$ can be deduced. By suitable integration of the observed values of $\mathrm{d}\lambda/\mathrm{d}T$, they obtained values of λ for tin several times higher than those of LAURMANN and SHOENBERG [41] (who used the Casimir method, in which the field, rather than the temperature oscillates, and changes of mutual inductance with temperature are measured), and it is probable that the discrepancy was due to imperfect specimen surface conditions. Their method has the disadvantage that (unlike the Casimir method), it does not directly show up the existence of slight normal inclusions, which may completely ruin the accuracy of the results; it is, moreover, technically rather complicated. More recently ŠARVIN [42] has repeated the experiment with some modification of the technique of oscillating the temperature and using better surface conditions; he now reports much better (though not complete) agreement with the data of LAURMANN and SHOENBERG. He also reports a field variation of λ of the form

$$\frac{d\lambda}{dT} = \left(\frac{d\lambda}{dT}\right)_{H=0}\left(1 + \alpha\left(\frac{H}{H_c}\right)^2\right), \tag{6}$$

from which it can be easily shown that

$$\lambda = \lambda_{H=0}\left(1 + \beta\left(\frac{H}{H_c}\right)^2\right) \quad \text{with} \quad \beta = \frac{1}{5}\alpha\,. \tag{7}$$

The experimental value of β was found to be 0.06; here again it is probable that the high value of β (cf. $\beta \sim 0.01$, as found by PIPPARD [72] using an R.F. method) is due to the appearance of normal inclusions when the field approaches H_c, and it is unlikely that ŠARVIN's value has any fundamental significance. It may be mentioned that Ginzburg and Landau's theory predicts a value of β only of the order found by PIPPARD.

8. – Theoretical Work.

The main theoretical contributions have been (*a*) the development of a new phenomenological theory of superconductivity by GINZBURG and LANDAU [73] which suggests a new interpretation of the properties of thin films etc., and of surface energy effects, and (*b*) a suggestion by LANDAU that since the number of superconducting electrons at 0 °K is only about a tenth of all the conducting electrons, while at the same time the R.F. behaviour indicates the absence of any conductivity of « normal » electrons at very low temperatures, the remaining electrons must be in « bound » states and should have a very high dielectric constant ε_0 (of order 10^8 to 10^{10} at 0 °K and decreasing to zero at T_c). This suggestion would modify the usual interpretations of the R.F. impedance of a superconductor, since the displacement current would not be negligible, as has hitherto been assumed.

The consequences of these new ideas have been worked out in various papers by GINZBURG, SILIN and ABRIKOSOV, and have been applied by ZAVARICKIJ and HAJKIN in the interpretation of their results. For a good general account of these theories see GINZBURG [74, 75, 76]. We shall now deal briefly with (*a*) and (*b*) separately.

(*a*) The phenomenological theory of F. and H. LONDON [77], though successful in giving a description of the Meissner effect and accounting at least qualitatively for the slight penetration of a magnetic field, does not give any natural explanation of the existence of a positive energy at the boundary surface between normal and superconducting phases; such a surface energy has, in fact, to be postulated *ad hoc*, as an additional assumption in order to explain the sudden, rather than gradual, disappearance of superconductivity at a critical magnetic field, and to explain the properties of the intermediate state, and various other phenomena. GINZBURG and LANDAU [73] have developed a new phenomenological theory designed to introduce a surface energy

more naturally, and to account better than the London's theory for the behaviour of specimens of very small dimensions (e.g. thin films). They introduce an « effective » wave function ψ of the superconducting electrons such that ψ^2 may be identified with n_s, the density of superconducting electrons, and they assume that the free energy in the absence of a field may be expanded in powers of $|\psi|^2$ in the immediate neighbourhood of T_c, and that it is sufficient to ignore powers higher than $|\psi|^4$. Minimization of the free energy with respect to $|\psi|^2$ then determines the equilibrium value of $|\psi|^2$ in terms of the coefficients of the expansion, and identification of the free energy with that of the normal state for $T = T_c$ relates the coefficients to the critical field of the bulk metal. In a magnetic field, considerations of quantum mechanics suggest that the free energy of the superconducting state should be increased not only by the usual term $H^2/8\pi$, but by a term depending on the gradient of ψ, and it is assumed that this extra term should have the form $\frac{1}{2m}\left(i\hbar\nabla\psi + \frac{e}{c}A\psi\right)^2$ (A is the vector potential of the field). Minimization of the free energy with respect to ψ and A, leads to two differential equations for ψ and A, rather than the single one for A of the London's theory (where the number of electrons is assumed constant and independent of field), and an expression for the surface energy is also obtained.

In these equations a parameter $\varkappa$ appears, defined as

$$\varkappa = \sqrt{2}\,\frac{e}{\hbar c}\,H_c\lambda^2\,, \tag{8}$$

where H_c is the bulk critical field and λ the penetration depth for small magnetic fields (note that close to T_c, $H_c\lambda^2$ is independent of temperature), and in the limiting case $\varkappa \to 0$, one of the differential equations leads to $|\psi|^2$ constant in space, while the other becomes the usual London's equation for field penetration, with a penetration depth which may, hovewer, depend on the value of the applied field (though it is constant in space). The general solution of the differential equations is much simplified by the fact that $\varkappa$ is very small (~ 0.1) for pure superconductors, and in these circumstances the differential equations may be solved approximately.

The solution for a semi-infinite superconductor bounded by a plane surface gives a field dependent penetration depth,

$$\lambda = \lambda_{H=0}\left(1 + \frac{\varkappa(\varkappa + 2\sqrt{2})}{8(\varkappa + \sqrt{2})^2}\left(\frac{H}{H_c}\right)^2\right), \tag{9}$$

which. as mentioned above, agrees better with Pippard's data than with those of Šarvin; the value of the surface energy α (expressed most conveniently in

terms of $\Delta = 8\pi\alpha/H_c^2$) is given by

$$\Delta = \frac{8}{3\sqrt{2}\varkappa}\lambda\,, \tag{10}$$

if it can be assumed that $\sqrt{\varkappa} \ll 1$. GINZBURG [76, p. 101] mentions that a more exact calculation by numerical integration leads to an appreciably lower estimate of Δ: for $\varkappa = 0.165$ he finds $\Delta = 6.2\lambda$, rather than 11.4λ from (10).

The solution for a thin film of thickness d is given in [73] and more fully discussed in a later paper of GINZBURG [78]; for thick films ($(\varkappa d/\lambda)^2 \gg 1$) the critical field h is given by

$$\frac{h}{H_c} = 1 + \frac{\lambda_{H=0}}{d}\left(1 + \frac{\varkappa(\varkappa + 2\sqrt{2})}{16(\varkappa + \sqrt{2})^2}\right). \tag{11}$$

For very thin films $\varkappa$ may be put equal to zero, since its influence is quite negligible, and h is given by

$$\frac{h}{H_c} = 2\sqrt{6}\,\frac{\lambda_{H=0}}{d}\,. \tag{12}$$

Calculation of the magnetization curves in this limiting case shows also that there is a critical thickness d_K given by

$$d_K = \sqrt{5}\lambda_{H=0}\,, \tag{13}$$

such that for $d > d_K$ destruction of superconductivity by a field is a first order transition accompanied by a sudden drop of magnetization and of $|\psi|^2$, while for $d < d_K$ the transition is second order with a smooth drop to zero of magnetization and $|\psi|^2$. Moreover, supercooling and superheating hysteresis effects can be expected for $d > d_K$, but not for $d < d_K$.

All these results for thin films (and also similar results for thin cylinders and small spheres, as worked out by SILIN [79], in as far as $\varkappa$ may be considered negligible (the term in $\varkappa$ in (11) amounts to only a few per cent), can be obtained also from the Casimir-Gorter theory if PIPPARD'S idea of long-range order or « coherence » [72, 80, 81], (see [82] for a general descriptive account) is introduced, i.e. if it is assumed that the number of superconducting electrons does not vary through the film (this is equivalent to the limit $\varkappa = 0$). Indeed close to T_c the Casimir-Gorter expression for the free energy becomes identical with the expansion of Ginzburg and Landau, so it is not surprising that the new theory leads to the same results. The new theory does not attempt to make predictions except close to T_c, but has the advantage that it makes

definite predictions about the magnitude of the long range order, and is thus able to predict the size of Δ (in order of magnitude agreement with experiment). The Casimir-Gorter theory on the other hand, by making a special and *ad hoc* assumption (designed to reproduce the known thermodynamic properties) about the form of the dependence of free energy on the number of superconducting electrons over the whole temperature range, is, together with the assumption of long range order, able to make predictions for thin films, etc., at all temperatures. Both theories are « two fluid » theories in the sense that they assume that the free energy is expressible as a function of only one extra parameter (the number of superconducting electrons or ψ^2) in addition to field and temperature, and the only real novelty of the new theory is the introduction of the « quantum mechanical » term which automatically produces the long range order which PIPPARD had to introduce as a purely empirical assumption. Because of this novelty, the new theory is able to make predictions about the size of Δ and the field dependence of λ (equations (10) and (9)), and it is by the truth of these predictions (which involve the finiteness of $\varkappa$) that the new theory must stand or fall; the other predictions such as equations (11) with $\varkappa = 0$, (12) and (13) are not really new, and their confirmation does not really prove the truth of the special assumptions of the theory. In fact the detailed analysis by GINZBURG [74] of the data on thin mercury films, by ZAVARICKIJ [40] of his data on thin tin films (see above) and by LOCK [39] of his data on magnetization curves of thin tin films, all confirm the predictions of both theories qualitatively, but cannot be made to fit completely quantitatively without rather forcing the data. As regards the values of Δ and the field dependence of λ, the predictions of equations (10) and (9) certainly agree with experiment in order of magnitude, but the experimental data are not yet good enough to say more. Thus, it would seem that the new theory is probably on the right lines in its general formulation, but it would not be too surprising if the detailed form of the assumptions it makes should prove too simple to give exact quantitative agreement.

GINZBURG and LANDAU [73] have also discussed destruction of superconductivity in thin films by a current in the limit $\varkappa = 0$, i.e. in the limit equivalent to the Casimir-Gorter theory plus long range order. They find, in qualitative agreement with ŠAL'NIKOV's data [37], that the critical current should be very small, but their discussion does not appear to take any account of edge effects, which should be important, since in the actual experimental conditions the current would tend to be concentrated in the film edges, while the discussion assumes a uniform distribution.

GINZBURG [83] has also shown how the theory has to be modified to take account of anisotropy, but his calculation is quite unable to account for the non-tensor character of λ, found experimentally by PIPPARD [49].

Recently ABRIKOSOV [44] has made an interesting suggestion of a possible

extension of the range of applicability of the new theory. He suggests that the unannealed films of tin and thallium studied by ZAVARICKIJ (see above) have values of $\varkappa > 1/\sqrt{2}$ (as might be the case if the penetration depth of the material in the disordered state of an unannealed film were somewhat higher than for pure strain free superconductors). For $\varkappa > 1/\sqrt{2}$ GINZBURG and LANDAU [73] showed that the surface energy becomes negative and superconductivity can persist above H_c; ABRIKOSOV solves the equations of the theory for arbitrary $\varkappa$ and obtains a relation of the form

$$\frac{h}{\theta^2} = f\left(\frac{1.28\cdot 10^{-4}}{\theta d}\right), \tag{14}$$

for the field h at which the superconductivity of a film of thickness d is completely destroyed, where θ is given by

$$\theta = \left(\frac{2e}{\hbar c}\right)^{1,2} H_c \lambda\,, \tag{15}$$

and f is expressed in terms of hypergeometric functions. Equation (14) reduces correctly to the theoretical predictions for small $\varkappa$, but for large $\varkappa$ leads to the prediction that, for $d \to \infty$, $h \to \varkappa\sqrt{2}H_c$, i.e. for $\varkappa > 1/\sqrt{2}$, $h > H_c$. From the general relation (14) ABRIKOSOV deduces values of θ appropriate to each of ZAVARICKIJ's films at each temperature, and hence obtains curves of θ against (T/T_c), which fit fairly well on a common curve if suitably scaled (i.e. if $k\theta$ is plotted where k is chosen for each film to give a definite value of θ at one value of T/T_c). This common curve agrees with the temperature variation indicated by (15) if H_c and λ are assumed to vary with temperature as for pure strain free superconductors. On the basis of this agreement with experimental data, ABRIKOSOV suggests that the known peculiarities of the « hard » superconductors and alloys may also be associated with values of $\varkappa > 1/\sqrt{2}$, and suggests the name « superconductors of the second group » for such superconductors.

(*b*) As explained above, LANDAU suggested (reported by GINZBURG [75]) that a large fraction of the free electrons (those that do not become « superconducting » electrons) enter into some kind of bound states when the temperature of a superconductor is lowered. It is to be expected that the frequencies characteristic of the binding would be of order of magnitude

$$\omega_0 \sim kT_c/\hbar \qquad (\sim 10^{11} \text{ to } 10^{12}) \tag{16}$$

so that at frequency ω the dielectric constant ε_0 associated with the bound

« normal » electrons should be of order

$$\varepsilon_0 = \frac{4\pi e^2 n_0}{m\omega_0^2} \quad (\sim 10^8 \text{ to } 10^{10}) , \tag{17}$$

for $\omega < \omega_0$. Since ε_0 is so large, the displacement current is no longer negligible, and in the expression for curl H in the equation governing the R.F. behaviour of the metal in the two-fluid model an extra term $i\omega\varepsilon_0 E$ has to be added, i.e. this becomes

$$\text{curl } H = \frac{4\pi}{c}\sigma E - \frac{ic E}{\omega\lambda^2} + \frac{i\omega\varepsilon_0}{c^2} E . \tag{18}$$

This equation can then be regarded as that appropriate to a metal of conductivity σ and effective dielectric constant ε, where

$$\varepsilon = \varepsilon_0 - \frac{c^2}{\omega^2\lambda^2} = \varepsilon_0 - \frac{4\pi e^2 n_s}{m\omega^2} . \tag{19}$$

Even though the R.F. frequencies ordinarily used in experimental work are such that $\omega \ll \omega_0$, n_0 is about ten times greater than n_s and thus ε_0 may not be negligible compared to $c^2/\omega^2\lambda^2$ in (19) (moreover, of course (17) only indicates a probable order of magnitude, and a numerical factor might make ε_0 even larger).

As is well known, however, the formulation expressed by (18) is, in fact, inadequate, since the anomalous skin effect must be taken into account. Ginzburg [84] has allowed for the anomalous skin effect in a simplified way by making some special assumptions (amounting to an extension of Pippard's « ineffectiveness concept ») and obtains an expression for the temperature and frequency variation of the complex impedance Z $(= R + iX)$ of the metal at radio frequencies. We need not, however, discuss his results, since a more general approach has been recently made by Abrikosov [53], who assume merely that the normal electrons in the superconducting state have a certain static conductivity σ, and mean free path l, and that the metal has an effective dielectric constant ε, and then rigorously applies the Reuter-Sondheimer theory of the anomalous skin effect to obtain an expression for Z. His results are expressed in such a way that σ/l and ε can be deduced from the observed values of R and X. The relevant formulae are

$$\frac{\sigma}{l} = \frac{2c^2}{3\pi^2\omega}\lambda^3(1+\eta) , \tag{20}$$

$$\varepsilon = \frac{c^2\lambda^2}{\omega^2}\lambda^2(\eta - 3) , \tag{21}$$

where for diffuse reflection of electrons at the metal surface

$$\frac{R}{X} = \frac{1}{2\pi}\left(2\sqrt{\eta}\ \mathrm{tg}^{-1}\sqrt{\eta} - \ln\frac{1}{4}(1+\eta)\right), \tag{22}$$

$$\lambda = \frac{2\pi\omega}{c^2}\,\frac{x}{x^2+R^2}, \tag{23}$$

(formulae are given also for specular reflection, but these are of little practical interest).

The difficulty in applying these formulae is that X cannot be measured directly in the superconducting state; if it is *assumed* in accordance with the prediction of the Reuter-Sondheimer theory for extreme anomalous conditions (and some of PIPPARD's results suggest that this is probably not valid) that in the normal state $X_n = \sqrt{3}R_n$, then X_s in the superconducting state can be inferred from the difference $X_s - X_n$. This is what HAJKIN [52] does, and finds (either from his own data or from PIPPARD's [49]) that ε_0 at 9 400 MHz is not only relevant, but is indeed the dominant term in (19). He gives a curve of ε_0 as a function of temperature which descends smoothly to zero at T_c (as is to be expected) from a value of about $5\cdot10^9$ at 2 °K. It is, however, not obvious how sensitive his analysis would be to any change from the doubtful assumption $X_n = \sqrt{3}R_n$

ABRIKOSOV also points out that for very thin films Z assumes a much simpler form; in fact, it can easily be shown that

$$\frac{1}{Z} = \sigma d + \frac{i\omega d}{4\pi}\,\varepsilon, \tag{24}$$

and HAJKIN [52] applying this to his results for thin films deduces a curve of ε_0 which agrees, at least qualitatively, for all his thin films with that for the bulk metal (exact comparison is complicated by the fact that the transition temperatures of his films are a bit higher than that of the bulk metal). The curves of σ as a function of temperature pass through a maximum just below T_c and then fall steeply towards zero as the temperature is lowered.

Although the introduction of ε_0 into the theory requires serious consideration, it is by no means certain that it is necessary, and indeed it would not be required in Pippard's new phenomenological theory [85]. HAJKIN appears to find the introduction of ε_0 necessary to account for the results at 9 400 MHz and finds ε_0 to be of the predicted order of magnitude, but it is quite possible that his argument would become invalid if X_n was appreciably larger than $\sqrt{3}R_n$, as PIPPARD suggests is the case; moreover, the introduction of ε_0 appears not to help in reconciling the predicted frequency dependance of resistance at low temperatures with experiment (taking into account any reasonable

frequency dependence of ε_0). As regards HAJKIN's thin film results, these could perhaps be interpreted as due to an increased value of λ in such thin films (though it would be puzzling then why λ was approximately the same for all the films studied), without introducing a high value of ε_0 at all. There is not yet enough experimental data (in particular on the frequency dependence of R) to settle these questions decisively, but whatever the truth of the matter should prove to be, the new theoretical ideas will have been of use if only in stimulating new experiments.

Finally, we should mention an interesting review by GINZBURG [76] of the microscopic theories of superconductivity in which *inter alia* he discusses the possibility of finding an « excitation spectrum » which would account for the facts of superconductivity in the same sort of semi-phenomenological way as does Landau's theory of liquid helium [86].

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Polish Physics.

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CONTENTS

1. Introduction. – **2. Guide to Bibliography.** 1. Relativity. 2. Molecular Physics. 3. Field Theory. 4. Counter Physics. – **3. Bibliography.**

1. – Introduction.

The following is based almost exclusively on papers published in the *Acta Physica Polonica* from Vol. **9**, n. 1 (1947) (the first post war issue) to Vol. **11**, n. 2, both inclusive. The printing of the last issue was completed on the 30th November 1952. The issues of the *Bulletin International de l'Académie Polonaise des Sciences et des Lettres* for the period 1947-50 were also inspected, but the papers published there are largely on subjects not directly related to physics.

These publications do not cover all the work done since the war by Polish physicists. A number of contributions from Polish authors have appeared in various Journals in England, America, Russia and Italy. The present review is confined to papers actually published in Poland.

The more active Polish centres of research in the past few years have been in Cracow, Warsaw, and the new University at Toruń. The trends in post-war physics in Poland fall into two fairly well defined classes. The first bear a genealogical relationship to pre-war work, mainly on molecular optics (e.g. A. PIEKARA at (Danzig and A. JABŁOŃSKI at Toruń) and relativity (J. WEYSSENHOFF at Cracow). Under the second heading one would include new developments in field theory (J. RAYSKI and J. RZEWUSKI at Toruń), experimental nuclear physics and cosmic rays (M. MIĘSOWICZ at Cracow, M. DANYSZ at Warsaw), though some work in these fields was done also before 1939. The output of papers from Poland since the war has not

been large, though it has been increasing steadily. The quality of the work done is not uniform. Due to the small number of physicists actively engaged in research there are usually only one or two working in a given field and their papers often appear to suffer from a lack of clarifying discussions and many-sided criticism.

In the years after the war there had been some personal contact between physicists from Poland and Western Europe, and a few of them spent some time abroad. (J. Blaton at Copenhagen, J. Rzewuski and B. Makiej at Birmingham, M. Günther at Leiden and Birmingham, J. Rayski at Zürich and M. Danysz at Bristol). In this respect the situation seems to have deteriorated in the past three years.

2. – Guide to Bibliography.

At the end of this article a numbered list of all the papers under review will be found in alphabetical order according to authors. In many cases the title is an adequate guide to the contents. In this section we shall give an outline of a few representative papers.

2·1. – *Relativity.*

We shall begin with articles falling into the first of the two classes mentioned above.

In the field of relativity there is a series of contributions by J. Weyssenhoff (in collaboration with a A. Raabe) and B. Średniawa [40, 41, 68-72], dealing with classical relativistic particles with spin. The motivation of these investigations is explained in the following remark in [70], p. 46.

« The view has been often expressed that some at least of the difficulties of the present quantum theory of fields arise from the inadequateness of the underlying 'classical model', rather than of the methods of quantization.... Perhaps some progress might be made by substituting a spin-particle obeying the laws of relativistic dynamics for the spinless particle used as a starting point by Dirac ».

Equations of motion for such a particle (also in the presence of an electromagnetic field) are derived and the case of motion with light velocity is treated separately. These models lead to a type of circular motion bearing a certain analogy to the quantum mechanical « Zitterbewegung ».

In a paper on general relativity [13] L. Infeld presents an application of the method of studying the equations of motion from the field equations (developed by Einstein and Infeld in 1938-1949) to Einstein's unified theory of 1950, in which gravitation and electromagnetic fields are treated simultaneously. The author finds that « unfortunately, the equations of motion remain Newtonian and are uninfluenced by the 'electromagnetic field' ».

2·2. – *Molecular Physics.*

In the field of molecular physics A. Piekara continues his pre-war investigations into phenomena of molecular orientation in polar liquids [35-37]. See also K. Zakrzewski and A. Piekara, *Bull. Mat. Acad. Pol. Sci. Lett.*, No. 4-10 A, 1939 (published in 1946). These papers present an extensive discussion of the interpretation of the following four phenomena of molecular orientation: 1) Electric polarization. 2) Electric bi-refringence. 3) The saturation of the dielectric constant and 4) Magnetic bi-refringence (Cotton-Mouton effect). An extension of Onsager's theory of dielectric polarization is attempted, whereby the action of the nearest neighbours would be taken into account individually and only the more distant parts of the liquid treated as a continuum. This leads, in particular, to various kinds of clusterings of molecules, or « couplings », of which three are discussed: 1) The coupling due to a directional field produced by the surrounding molecules ordered in a momentary lattice. 2) The coupling between two polar molecules. 3) The coupling between two anti-parallel pairs whose resulting moments are coupled parallel. Comparison with experimental data on nitro-benzene is disscused and a satisfactory interpretation appears to be possible on the basis of the above couplings.

The theory is applied in [37] to the calculation of the lowering of the freezing point of dilute solutions of polar substances in non-polar solvents.

Still in the field of molecular optics two papers by A. Jabłoński [16, 17] and one by Wanda Hanus [10] treat the depolarizing effect of the torsional vibrations of molecules on the luminescent radiation emitted by them. A comprehensive quantum-mechanical treatment of a torsional oscillator is given in [10], extending the theory of L. Pauling *Phys. Rev.*, **36**, 430 (1930)) and T. E. Stern (*Proc. Roy. Soc.*, A, **130**, 551 (1931)) to molecules possessing three different principal moments of inertia. The exact treatment is confined to small oscillations, non-linear terms being evaluated by perturbation theory. The way of correlating the observed depolariation with the mean angle of turn of the molecules and other properties of the oscillators is developed and application to the fluorescence of glycerine solutions of fluoresceine and benzene seem to lend support to this general interpretation of the effect.

The two papers by M. Puchalik [37 and 38] are accounts of experimental work on the dipole moments of carbonyl cyanide and some members of the homologous series $C_5H_9(CH_2)_nCl$, $C_6H_5(CH_2)_nCl$ and $C_6H_{11}(CH_2)_nCl$, and the temperature dependence of the dipole moment of benzyl chloride.

Finally, the two papers by J. Rzewuski [56] and J. Dąbrowski [2] can be traced to the pre-war school of spectroscopy whose leaders were A. Rubinowicz and J. Blaton.

2·3. – *Field Theory.*

Coming now to field theory, there is a series of contributions by J. Rzewuski and J. Rayski on electrodynamics and meson theory [42-51, 56-63]. In paper [57] J. Rzewuski calculates by perturbation theory the differential cross-section for the radiactive collision between two particles obeying the Dirac equation, the interaction being static. When one of the particles is infinitely heavy the formulae reduce to those of H. Bethe and W. Heitler (*Proc. Roy. Soc.*, **146**, 83 (1934)). For equal masses and large energies the cross-section has the same order of magnitude as their expression for bremsstrahlung.

Later on both Rzewuski and Rayski concentrated on the problem of divergencies in field theories. In paper [42] J. Rayski discusses various relativistic form-factors introduced by means of operators of the form $\exp[\alpha^2\Box]$, $\exp[-\alpha^4\Box^2]$, $1/(1-\alpha^2\Box)$, $1/(1+\alpha^4\Box^2)$, where $\Box$ is the d'Alembertian operator and α a constant. In Paper [43] (work done in Zürich) J. Rayski studies the problem of the simultaneous interaction of several fields within the framework of the Heisenberg-Pauli formalism. It is an extension of the investigations of A. Pais (*Kon. Ned. Akad. Verk.*, **19**, No. 1 (1947)) who introduced a coupling of a spinor field with a neutral meson field. The view is taken that it may not be possible for electron theory to stand alone and that problems of electron structure may involve mesons, neutrons, etc. The need for some such mixture is suggested even in the classical theory of the electron where cohesive non-electromagnetic forces are necessary to ensure the stability of a small charge distribution. In paper [43] the interest centres on the problem of vacuum charge fluctuations. It is found that for a suitable mixture of charged spinor and scalar fields the photon self-energy may be made to vanish to second order in e^2.

These investigations were continued with J. Rzewuski in [50], where an attempt is made to find a combination of several fields which will mutually cancel out divergencies. It is found that a system consisting of an ingenious mixture of a photon, an electron, a neutral scalar meson and two charged scalar meson fields is free of divergencies of the mass-renormalization type.

In paper [46] Rayski considers the scattering on one another of scalar neutral particles with vanishing rest mass, arising in virtue of their coupling to a complex scalar field. In part II of this work [51] (with B. Średniawa) the more realistic example of the scattering of light by light is treated by the Feynman and Dyson technique.

In papers [59] (J. Rzewuski) and [48] (J. Rayski) Feynman's methods of 1949 are used to study the quantization of the Peierls-McManus classical theory of the electron and other types of extended source theories. Interest

in extended source theories was further stimulated by the «non-local» fields introduced, at about this time by M. Born and H. Yukawa. Thus paper [49] by Rayski follows on his publication in *Proc. Phys. Soc.* (London), **64**, 951 (1951) in which the ideas of non-localizability and reciprocity were applied to two coupled scalar fields. In paper [49] the main concern is with non-local electrodynamics.

2·4. – *Counter Physics.*

In the field of nuclear physics the work done in Poland has so far been confined to experiments with natural sources of accelerated particles: cosmic rays and radioactive sources. No papers in theoretical nuclear physics have appeared.

Work in cosmic ray physics was resumed after the war at the Physical Laboratory of the Mining Academy in Cracow. In a series of papers [22, 23, 30] M. Mięsowicz, L. Jurkiewicz and J. M. Massalski investigated the question of the origin of a soft, low ionizing radiation at dephts down to 660 m water equivalent, first studied by Barnóthy and Forró in 1939. They arrive at the conclusion that this radiation is due to radioactivity of local origin.

More recently cosmic ray work by the photographic plate technique appears to have been started (see a note by Danysz and Pniewski in *Phil. Mag.*, **44**, 348 (1953)).

An interesting experiment with neutrons from a Ra-Be source is reported by J. A. Janik in [20]. Absorption measurements of slow neutrons in concentrated solutions of H_2SO_4 were found to reveal the effects on the scattering cross-section of the electrolytic dissociation and of the hydration of the H_2SO_4 molecule. This is an example of the well known effect of the chemical binding on the cross-section, interpreted by Fermi in 1936.

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Recent Research on Cosmic Radiation in the Soviet Union.

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(ricevuto il 7 Dicembre 1953)

CONTENTS

1. Introduction. – 2. Reviews of some Papers on Cosmic Radiation.

1. – Introduction.

In June 1952 a Conference on Cosmic radiation was held in the Soviet Union and, since (because of the war) no meeting on this subject was held in the previous fifteen years, the papers presented at this Conference had not only the purpose of communicating new results, but also of reviewing the work done during that period. Therefore it seemed advisable to the reviewer to give a short account on the principal experimental results reported at this meeting and to summarize briefly the theoretical papers.

It is well known that the solution of fundamental theoretical problems depends on the study of particles at extremely high energies ($\sim 10^{16} \div 10^{18}$ eV). Thus the discovery of new and important features of very high energy extensive showers reported at this Conference by several authors (*), appears to be the main contribution obtained. Also the theoretical description of the cascades of nucleons, mesons and electro-photonic component presented at the meeting represents a great progress in our understanding of these high energy events.

All papers reported in the following are published in a special issue of *Izvestija Akademii Nauk SSSR, Ser. Fiz.* **17**, n. 1 (1953).

(*) See the communication of G. T. ZACEPIN, I. L. ROZENTAL', L. I. SARYČEVA, G. B. HRISTIANSEN, L. H. ÉJDUS.

2. – Reviews of Some Papers on Cosmic Radiation.

D. V. SKOBEL'CYN (Chairman of the Conference): **Summary of communications presented at the June 1952 Meeting on Cosmic Rays: introductory remarks.**

After having recalled that, because of the war no meetings on this subject have been held for more than 15 years, Professor SKOBEL'CYN stresses the increasing importance of research in the field of cosmic radiation. The fundamental subject of these studies is the discovery of new elementary particles and the study of their interactions. These problems are far from being solved and one may expect that new important discoveries will be made. In the last ten years the great progress in experimental knowledge has not been accompanied by a similar progress of the theory. Important results have been achieved with the use of photographic emulsions introduced by the soviet physicists in the study of the cosmic rays.

SKOBEL'CYN remembers the contribution of soviet physicists to the discovery of the nucleonic component and of the so called « nucleo-electronic » showers, i.e. showers containing nuclei, mesons and a cascade component of electrons and photons. SKOBEL'CYN refers to the works of VEKSLER, ŽDANOV and LJUBIMOV performed at Pamir in 1945-46, who have studied the production of these showers by separating the electron-photon component from the component of protons and charged mesons.

The origin of the electron cascade component has been finally explained after the discovery of the very short-lived neutral meson decaying in two photons.

Important indications on the high energy primary particles, derive from the study of these showers. Their variation with atmospheric depth and with latitude allows to draw some conclusions on the absorption of the primary radiation. The absorption curves, in fact, can be interpreted in agreement with the nucleon cascade theory proposed by G. T. ZACEPIN.

Most of the nucleons observed in this way have energy of the order 10^{10} eV, and the collision cross-section in the neighbourhood of this energy has been estimated. With the use of the photographic emulsions some nuclear collisions with energy of 10^{13} eV have been observed. From the study of extensive showers some information on particles with energy ranging from 10^{15} to 10^{18} eV can be drawn. The research in this field is very important and requires new techniques.

These results show that the theoreticians have the task of discovering new laws holding in the range of these extremely high energies.

SKOBEL'CYN refers briefly to the well known theory of Fermi on the multiple production of mesons stating that also in the Soviet Union the theoreticians are studying this problem.

The soviet physicists are also studying the nature of the primary radiation and the time variations of the different components in connection with the problem of the origin of the cosmic radiation.

C. N. Vernov, A. M. Kulikov and A. N. Čarahč'jan: **Nature and properties of the prymary Cosmic radiation.**

The authors have studied the penetrating component (traversing 10 cm of lead) and the « nucleo-electronic » showers in balloon flights at the altitude of 20 km and three different latitudes (51°, 31°, 2°).

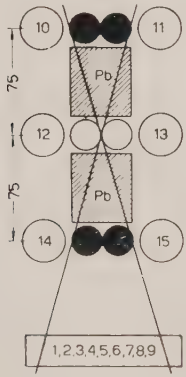


Fig. 1. – Counter arrangement. Counters indicated in black register two-field coincidences, others form a hodoscope. The lead filter is 10 cm thick.

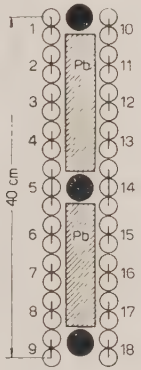


Fig. 2. – Counter-arrangement in the apparatus. The black counters register a threefield - coincidence, others are a part of the hodoscope. The thickness of the lead filter is 32 cm.

The report begins with a reference to results obtained in previous studies (1945-48). These can be summarized as follows: most of the primary particles are protons; the electron-photon cascade component is due to very short-lived particles produced in the upper layers of the atmosphere (Vernov: *Žu. Eksper. Teor. Fiz.*, **15**, 621 (1949)); a 10 cm screen of lead in the high atmosphere eliminates most of the electrons, leaves μ-mesons unaffected and interacts strongly with protons.

The set up of Geiger counters and lead screens is shown in figs. 1 and 2. Each counter was connected to a 20-channel hodoscope. The signals

transmitted by radio were received on the screen of an oscillograph and recorded photographically.

On the whole 18 ascents have been performed with the device of fig. 1. Of these ten at Moscow (51° lat.), five at 31° latitude and three at the equator.

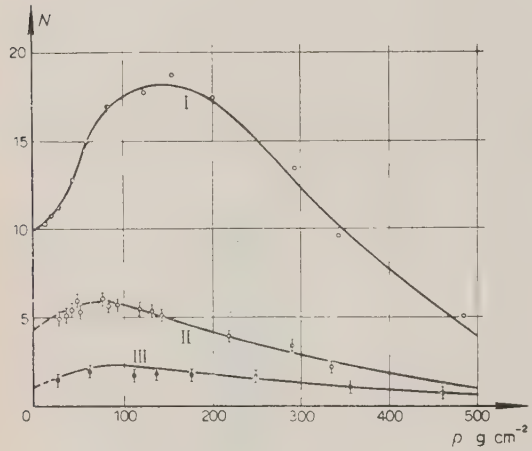


Fig. 3. – Frequency N of particles ($min^{-1}\,cm^{-2}\,sterad^{-1}$) in function of the atmospheric depth at the latitude 51° Nord; curve I: without supplementary filter; curve II: particles going trough 10 cm Pb without producing nucleon-electron showers; curve III: particles going trough 32 cm Pb without generating such showers.

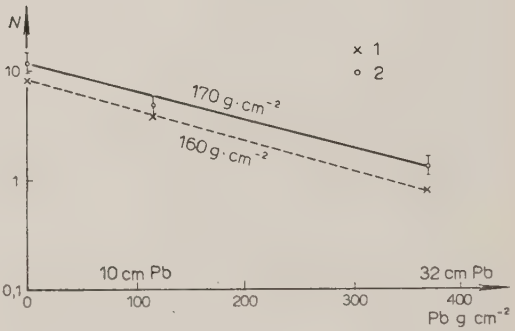


Fig. 4. – Dependence of the absorption of particles from the thickness of lead filter in the telescope: 1. measurements at 25 km height; 2. results obtained from the extrapolation at the limit of the atmosphere. The number of in particles is given $min^{-1}\,cm^{-2}\,sterad^{-1}$.

With the device of fig. 2 three ascents occurred at Moscow and two at 31° latitude.

Figs. 3, 4, 5, 6, 7 show the results. The collision cross-section is deduced to be approximately geometrical for protons of $5 \cdot 10^9$ eV against lead nuclei.

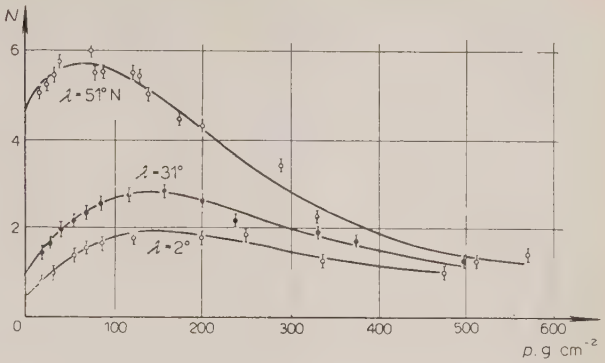


Fig. 5. – Number N (min $^{-1}$ cm $^{-2}$ sterad $^{-1}$) of particles going trough 10 cm Pb without multiplication in function of atmosphere depth at geomagnetic latitudes 51°, 31° and 2° Nord.

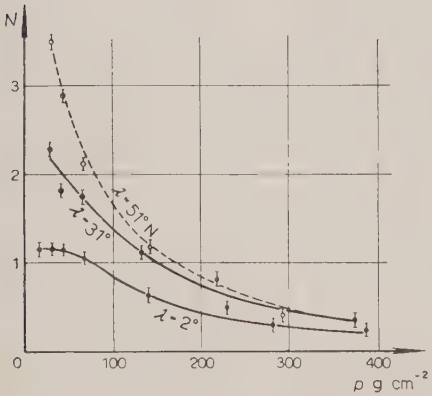


Fig. 6. – Number N (min^{-1} cm^{-2} sterad^{-1}) of electron-nucleon showers in function of the atmosphere depth p at geomagnetic latitudes 51°, 31° and 2° Nord.

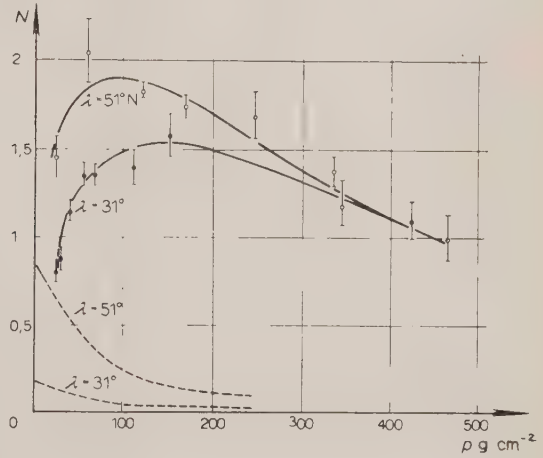


Fig. 7. – Number N (min $^{-1}$ cm^{-2} sterad^{-1}) of particles going trough 32 cm Pb without generating nucleonic showers, in function of the altitude. The lower curves represent protons which have not suffered nucleon reactions in 30 cm Pb.

N. L. GRIGOROV and V. S. MURZIN: **Interaction of primary particles of different energies with matter.**

The Authors have studied the latitude effect at different altitudes by means of balloons equipped with ionization chambers and other different devices reproduced in figs. 8 and 9 for the study of the showers of nucleons and electrons.

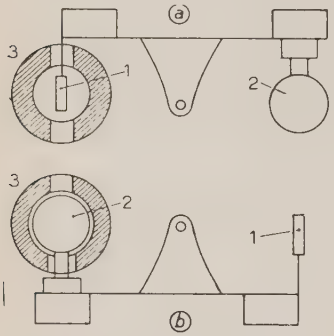


Fig. 8. – Arrangement used to study the transition effect air-lead: 1) counter, 2) ionization chamber, 3) lead filter. Arrangement *a* serves to measure number of particles below the filter and ionization current without filter; arrangement *b* measures ionization below the filter and particles without.

The measurements have been performed in the stratosphere at geometric latitudes 51° and 31°. Part of the results are summarized in figs. 10 and 11 and in tables I and II. Finally the ionization burst have been measured by means of ionization chambers surrounded by counters connected to an hodoscope, with the aim of investigating the process of burst formation and the relative importance of stars and showers in producing the burst. The results of these measurements (performed at latitudes 2°, 31° and 51°) are shown in fig. 12. The authors draw the following conclusions:

1) Primary particles with energy $\sim 3 \cdot 10^9$ eV lose in traversing the whole atmosphere about 35% of their energy in

TABLE I. – *Amount of energy lost in the production of electron-photon component.*

Energy		Energy, E_0, of primary particles (eV)	
		$1.5 \cdot 10^9 < E_0 < 7 \cdot 10^9$	$E_0 > 7 \cdot 10^9$
given to the electron-photon component in the whole atmosphere, eV cm^{-2} s^{-1}		$(2.3 \pm 0.15) \cdot 10^8$	$(7.2 \pm 0.3) \cdot 10^8$
given to the electron-photon component in nuclear interactions, referred to 1 primary particle	in the whole atmosphere. ε_0	$(0.48 \pm 0.03) \cdot 10^9$, *i.e.* 17% E_0	$(6.7 \pm 0.3) \cdot 10^9$ *i.e.* 40% E_0
	in the first collision, ε_1	$(0.30 \pm 0.04) \cdot 10^9$, *i.e.* 11% E_0	$(2.1 \pm 0.2) \cdot 10^9$, *i.e.* 13% E_0
	$\varepsilon_1/\varepsilon_0$	(63 ± 10)%	(31 ± 4)%

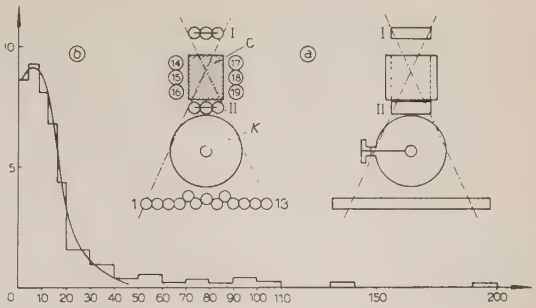


Fig. 9. – Arrangement used to study the electron-nucleon showers at the latitude 31° Nord. Groups of counters I and II give rise to two-field coincidences: *C* is a 10 cm thick lead filter; the counters 1-13 form a hodoscope. *K* is a ionization chamber. Curve *b* gives the results obtained at the altitude 20÷23 km (frequency of showers in function of the burst-size in units of probable ionization of one relativistic particle).

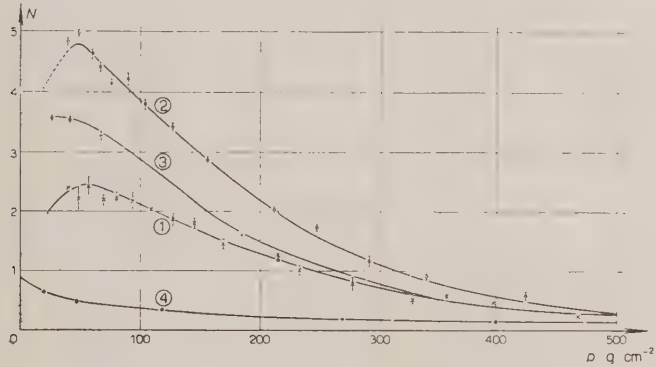


Fig. 10. – Total flux of particles in function of the altitude obtained at 51° N: 1) in the atmosphere; 2) below a filter of 1-2 cm Pb; 3) below a filter of 4 cm Pb; 4) hard component from data of VERNOV and KULIKOV (1950).

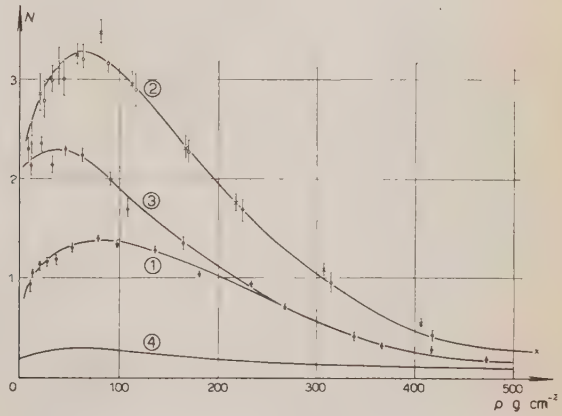


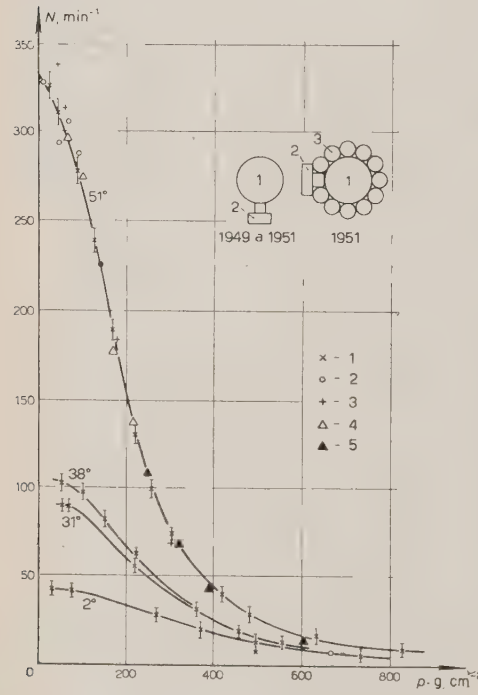
Fig. 11. – Number of particles in function of atmospheric depth at 31° Nord.

TABLE II.

Fraction of the energy spent by the primary particles in generating different components.

Average energy of primaries, $\bar{E}_0$	$2.7 \cdot 10^9$ eV	$16.7 \cdot 10^9$ eV
Production of μ-mesons	$(0.96 \pm 0.06) \cdot 10^9$ eV, *i.e.* $(34 \pm 3)\%\ \bar{E}_0$	$(13.4 \pm 0.06) \cdot 10^9$ eV, *i.e.* $80\%\ \bar{E}_0$
Creation of heavy particles in stars	$(1.7 \pm 0.2) \cdot 10^9$ eV, *i.e.* $(61 \pm 6)\%\ \bar{E}_0$	$(3.3 \pm 0.6) \cdot 10^9$ eV, *i.e.* $20\%\ \bar{E}_0$
Ionisation	$0.12 \cdot 10^9$ eV, $\sim 5\%\ \bar{E}_0$	$\sim 0.2 \cdot 10^9$ eV, $\sim 0\%\ \bar{E}_0$

the production of π-mesons, and about 60% in the production of heavily ionizing particles (stars).



2) Primary particles wit h energy $\sim 20 \cdot 10^{10}$ eV lose in the atmosphere 80% of their energy in the production of π-mesons and 20% in stars.

3) Particles of energy $\sim 3 \cdot 10^9$ eV produce in the average one meson for collision. Particles of energy $\gtrsim 20 \cdot 10^{10}$ eV give rise

Fig. 12. — Variation of burst-frequency with atmosphere depth at various latitudes (measured with ionization chamber and hodoscope counters): × 1) indicates burst with more than $25 \cdot 10^3$ ion pairs; ○ 2) number of «stars» with more than 3 rays; + 3) burst with $210 \cdot 10^3$ ion pairs (1 primary α-particle); △ 4) burst measurements by McCLURE and POMERANTZ: *Phys. Rev.*, **79**, 911 (1950); ▲ 5) frequency burst with $210 \cdot 10^3$ ion pairs measured by BRIDGE and ROSSI: *Phys. Rev.*, **71**, 379 (1947).

already to nucleonic cascades. In the first collision about 25% of the energy of the primary particle is transferred to π-mesons.

4) Protons of energy $\sim 20 \cdot 10^{10}$ eV produce in the atmosphere secondary particles, which, in their turn, are able of producing mesons.

5) The energy acquired by neutral mesons is of the same order of the energy acquired by charged mesons.

6) The energy lost by primary particles in the first collision for the production of neutral mesons is about $10 \div 15\%$ and does not depend much on the primary energy in the range $3 \cdot 10^9 \div 20 \cdot 10^9$ eV.

G. T. Zacepin, I. L. Rozental', L. I. Saryčeva, B. G. Hristiansen and L. H. Ėjdus: **Nucleon interactions at high energies and extensive showers.**

The lack of experimental data on extensive showers had been pointed out in 1945 by Skobel'cyn who organized a program of research on this subject from 1946 to 1951 at Pamir (altitude 3 860 m) and at Moscow. Density spectra, variation with altitude and space distribution of particles in extensive showers have been studied. Since 1948 also the experiments of Vernov in the stratosphere, and of Veksler and Dobrotin on the

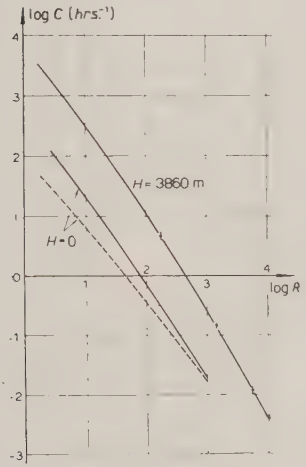


Fig. 13. - Integral spectrum of densities C (per hours) of extensive showers at 3 860 m and at sea level.

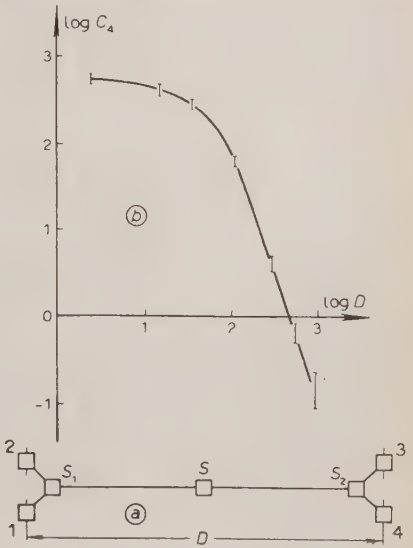


Fig. 14. – (*a*) Arrangement for the study of the spacial distribution of particles. (*b*) C_4 is the frequency of four-fold coincidences registered by S plotted against the distance D.

showers of nucleons, mesons and electrons have been performed in parallel with this research.

In the first experiment the frequency of showers as a function of the electron density has been measured by using the method of varying the surface of counters, in the range 1,5 - 8000 cm². The results of measurements at 3860 m and at sea level are shown in fig. 13. In this figure the dotted curve represents the frequency of showers at sea level deduced from electron cascade theory with an integral primary spectrum of the form $\sim E^{-1}$. The disagreement (by a factor 4) is striking particularly at low densities.

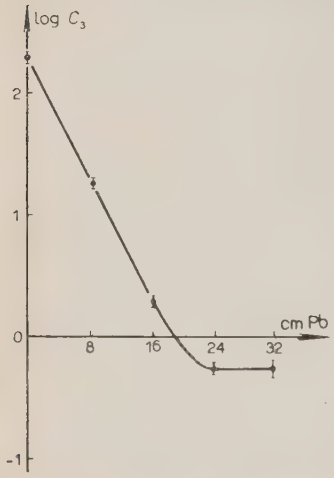


Fig. 15. Absorption of particles of extensive showers in lead.

In 1946-47 the frequency of extensive showers has been measured as a function of the distance D between the external counters, by means of the arrangement shown in fig. 14. The results are reproduced in the same figure for D ranging from 2 to 1000 m. In the range 100 to 1000 m the frequency can be given as a function of the distance D by the law $\sim D^{-K}$ with $K = 2.7$.

Another esperiment records the triple coincidences between three sets of counters at a distance of 1.5 m from one another. The sets were shielded with a variable thickness of lead and the corresponding frequency variation was measured.

The result is shown in fig. 15; one notices that for a thickness ranging from 0 to 20 cm of lead the frequency decreases (exponentially) by a factor ~ 200, and then it remains constant up to 32 cm Pb. In course of this experiment the presence of about 1.5% of penetrating particles in the central region of the shower has been recorded.

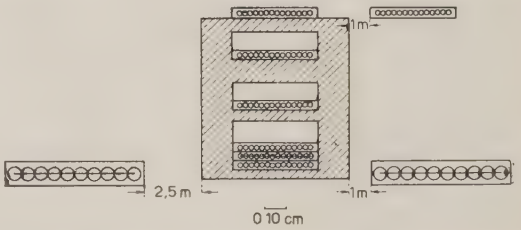


Fig. 16. – Arrangement for the study of the component generating nucleon showers in extensive showers.

Since 1948 the arrangement of counters with hodoscope shown in fig. 16 has been operated to study the interactions of penetrating particles, and the origin of the meson and electron components. These experiments as well as

those by COCCONI-GREISEN and COCCONI-TONGIORGI (1949) have confirmed the expectation of theoreticians about the existence of nucleon cascade showers. In 1949 ZACEPIN has shown that the electron-photon component in the extensive showers is originated in the upper layers of the atmosphere, and has given the foundations of a theory of the showers of nucleons and electrons. In 1948 also the density spectrum of penetrating particles in extensive showers has been measured at Pamir and also for these particles a power law spectrum has been found to fit the results with the same exponent, within an accuracy of 7 % of the total density spectrum.

From the theoretical analysis of this result the conclusion can be drawn that only a small amount of the energy of primary particles is transferred to neutral mesons and that in high energy collisions a multiple production of particles must occur.

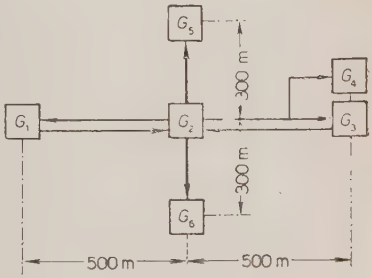


Fig. 17. – New arrangement for extensive showers. G_1-G_6 contain counters used for master 6-field coincidences. All sets G contain hodoscopic counters for determination of the local densities.

A second series of measurements has been performed with the arrangement shown in fig. 17. A new counting device has been designed to measure the space distribution of the particles density for each shower.

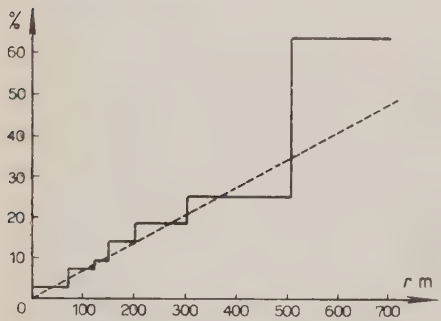


Fig. 18. – Variation of the fraction of penetrating particles from the distance r from the axis.

The use of the hodoscope technique, elaborated by L. N. KORABLEV, allowed to detect the number and the position of the counters of different surface discharged by each shower. By means of this device the axis of the extensive shower can be located and the density measured as a function of the distance from the axis. The experiments performed in 1949-51 show that the density of charged particles at great distances from the axis (200 ÷ 600 m) varies as r^{-n} with $2.7 < n < 3.1$.

The results for the penetrating component are striking. At the altitude of 3 860 m in the core of the shower ($r < 50$ m) the fraction of penetrating particles is 1.5 %; for $200 < r < 300$ it becomes 10 % and for $500 < r < 700$

it amounts to 25%. The average ratio between penetrating particles and electrons is 4-5%.

Similar measurements (*) at Moscow (s.l.) yield the results shown in fig. 18. At a distance from the axis of about 500 m the fraction of penetrating particles reaches 60%, while the average is 8÷10% of the total number of charged particles. Since the energy of an electron can be estimated to be $\sim 10^8$ eV, and that of one meson $\sim 10^9$ eV, one deduces that the total energy carried by the penetrating component is of the order or greater than the energy of the electron-photon component. These results hold for showers of more than 10^7 particles.

The following conclusions are also drawn in the present work. The integral energy spectrum of primary radiation can be expressed by a power law $\sim \varepsilon^{-\gamma}$ with $1.6 < \gamma < 1.8$ up to energies of 10^{18} eV, and the collision cross-section is found to be of the order of the geometric cross-section: $\sigma \sim 0.7\ \sigma$ geom. This results follow from the frequency variation of showers with atmospheric depth according to an exponential law with absorption free path of ~ 100 g/cm^2.

Furthermore a multiple production of particles must occur in nucleonic collisions with a multiplicity increasing with energy. For energies $10^{13} \div 10^{14}$ eV the multiplicity is $n > 5$.

The amount of energy transferred to neutral mesons is not higher than 20%, and therefore assuming that an equal share is given to charged mesons of both signs one deduces that a considerable amount of energy must be carried away by particles other than π-mesons. In the collision the particle distribution in the center of mass system is anisotropic.

L. D. Landau: **On the multiple production of particles in high energy collisions.**

The author consider Fermi's theory of multiple production suggesting a new treatment based on the following assumptions.

It is assumed that during the collision many particles are created in a volume whose transverse dimensions are of the order of the range of nuclear forces, contracted as in Fermi's theory according to the energy of the colliding particles. The author points out that during the formation of mesons the number of particles is undetermined, because the interaction between them is assumed to be so strong that their mean free path is small in comparison with the dimensions of the volume. The process of meson production is therefore compared with the motion and dilatation of an ideal (non viscous) liquid. The number of particles is determined when their relative distances increase

(*) L. H. Ějdus, M. I. Adamovič, I. A. Ivanovskaja, V. S. Nicolaev, M. S. Tuljankina: *Žu. Eksper. Teor. Fiz.*, **22**, 440 (1952).

beyond the range of interaction, and the particles become free. This happens when the mean free path is comparable with the dimensions of the system. LANDAU assumes the temperature at this moment to be $T_\mu \sim \mu c^2$ where μ is the pion mass.

To study the expansion of the liquid at temperature $T \gg \mu c^2$ the authors uses the equation $p = \varepsilon/3$ where p is the pressure and ε the energy density. The chemical potential ζ vanishes because the number of particles is undetermined:

$$\zeta = \varepsilon - Ts + p = 0 .$$

In this way the total number of particles is $N \sim K(E/2Mc^2)^{\frac{1}{4}}$ where E is the energy of the colliding particles in the center of mass-system, M is the nucleon mass, and K is a constant of the order of 2.

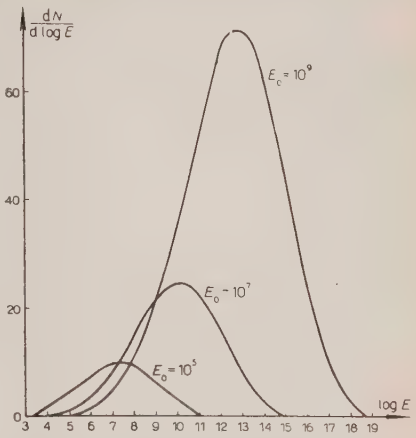


Fig. 19. - Differential spectra of secondary particles. Areas are proportional to the total number of particles (mesons and nucleons).

The author calculates also the angular distribution and the energy spectrum of the created particles, and discusses the case of the collision between nuclei.

In fig. 19 the differential spectrum of secondary particles is reproduced.

I. L. ROZENTAL': **On the theory of nucleonic cascades and the extensive showers.**

The author gives a theory of nucleonic cascades, assuming the multiple production in the collision of energetic nucleons.

He assumes also that the interaction mean free path for energetic nucleons is nearly equal to the geometrical one (the value used is ~ 80 g/cm^2 in air) and that the cross-section of mesons with nuclei is also geometrical. Then he writes and solves the diffusion equations.

From the comparison with the experiments the author concludes that the multiplicity increases with the energy of the primary particles as $n \sim E^\gamma$, where $\gamma \cong 1/4$ (as in Fermi's theory).

He concludes that this theory gives a satisfactory description also of the observed spacial distribution of particles in the extensive showers (*).

(*) *Žu. Eksper. Teor. Fiz.*, **23**, 440 (1952).

A. T. Dadajan and G. I. Merzon: **Spectrum and interaction with matter of proton in cosmic radiation.**

The measurements reported in this work have been performed in Caucasus (Mount Alagez 3200 m) with the experimental arrangement illustred in fig. 20. They improve the previous experiments performed with the methods introduced by A. I. Alihanov, A. I. Alihanjan and S. N. Nikitin in the years 1944-51. A 76 ton electromagnet with pole pieces of 100×30 cm and a gap of 12 cm has been used. A maximum field of 19000 örsted

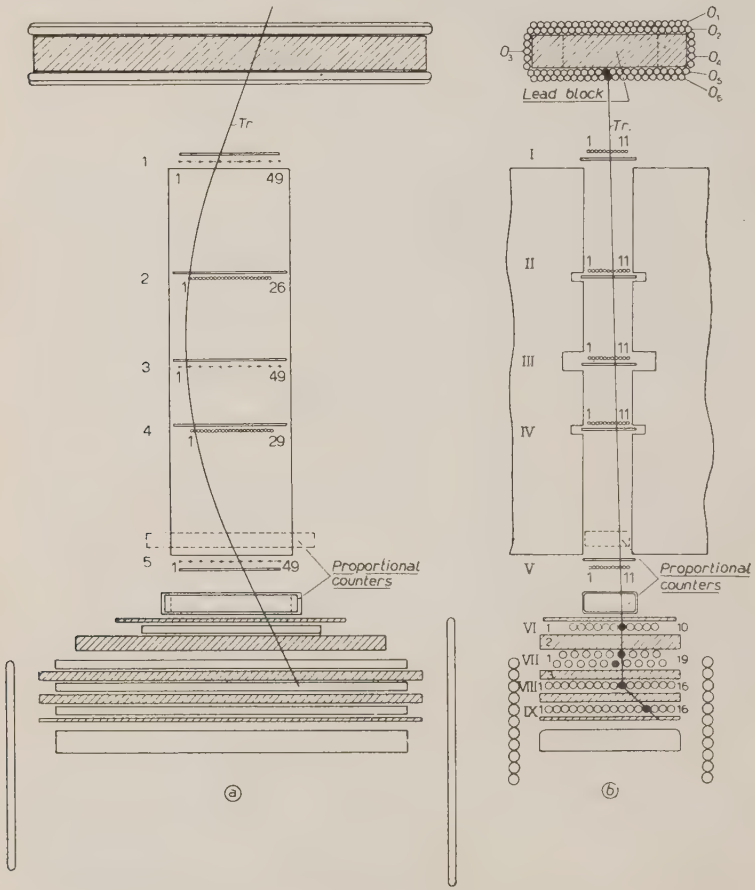


Fig. 20. Magnetic spectrometer (counter trays, proportional counters, and lead filters are indicated).

was available. Trajectories were determined by means of five sets of counters placed with the axis parallel to the magnetic field and five sets with the axis normal to the field. Each set contained 49 counters (diameter 4.6 mm, length 105 mm and aluminum wall 1/10 mm thick).

In fig. 21 the spectrum of particles produced in lead and in fig. 22 the spectrum of protons produced in lead are shown.

All these spectra can be well represented by a power law with exponents of the order of 2.8 and 3.8 for curves 1 and 2 of fig. 21 respectively, and 2.8 for the high energy protons of fig. 22, in agreement with the results of M. G. Milroy and J. G. Wilson.

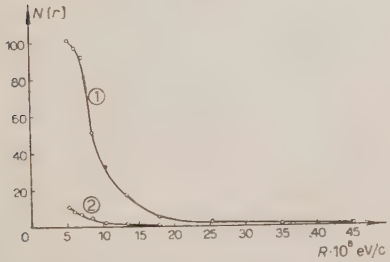


Fig. 21. Curve 1: spectrum of positive particles generated in Pb. Curve 2: negative particles.

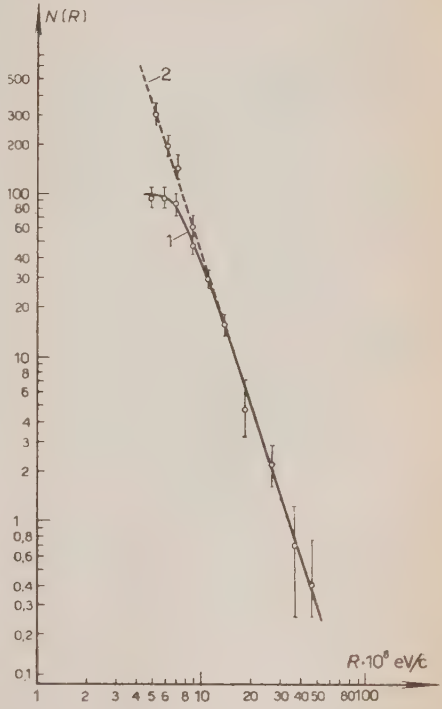


Fig. 22. Spectrum of protons generated in lead.

S. A. Azimov, N. A. Dobrotin, A. Z. Ljubimov and K. P. Ryžkova: **On the absorption and interaction particles producing showers of nucleons and electrons.**

The authors intend to measure the interaction free path and the absorption free path particles producing showers of nucleons and electrons. In fig. 23 the experimental set-up is shown containing 270 counters connected to a hodoscope. Each counter is connected to a neon lamp and the whole arrangement is triggered by a master pulse.

For nucleons with energy 10^{10} eV in carbon the resulting interaction free path is $\lambda_{int} = 70 \pm 7$ g/cm^2.

In order to obtain from the measurements the absorption mean free path λ_a the authors make use of the following relationship $\lambda_{int} = \lambda_a(1 - \bar{s})$, where $\bar{s}$ is the average number of secondary particles generated in the collision which are still able to produce new showers in the absorber.

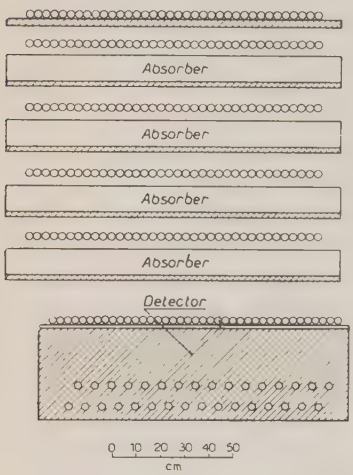


Fig. 23. – Arrangement used to measure the interaction mean free path.

In the present experiments the authors take into account the so-called density effect due to the possibility that the detecting apparatus may record showers produced simultaneously by two or more particles. The absorption mean free paths, corrected for the density effect have been measured for carbon, iron and lead with the following results:

$$\lambda_a^C = 216 \pm 15 \quad \text{g}\cdot\text{cm}^{-2}$$

$$\lambda_a^{Fe} = 344 \pm 25 \quad »$$

$$\lambda_a^{Pb} = 482 \pm 31 \quad »$$

The authors draw the following conclusions:

1) The absorption mean free path in carbon is in agreement with the results of measurements in water performed by AZIMOV and VIŠNEVSKIJ and is considerably larger than the absorption free path in air (~ 120 g/cm^2). The difference is tentatively ascribed to the decay of some showers producing secondary particles. The fraction of these unstable particles can be evaluated.

2) The absorption in lead is considerably smaller than in a carbon layer of equal mass (and therefore number of nucleons). Furthermore such absorption is approximately equal in carbon, iron and lead for layers proportional to their respective interaction free paths. This means that absorption is determined by the number of nuclei rather than by the number of nucleons.

3) The absorption free path for these elements is about three times the interaction free path:

$$\left(\frac{\lambda_a}{\lambda_{int}}\right)_C \sim \left(\frac{\lambda_a}{\lambda_{int}}\right)_{Fl} \sim \left(\frac{\lambda_a}{\lambda_{int}}\right)_{Pb} \sim 3\,,$$

This means that absorption occurs in the average after three interactions with nuclei.

An approximate evaluation of the number of secondary particles produced in each collision leads to the value ~ 1.

The authors conclude that the preceding results can only be explained by assuming that nucleonic cascades occur partially inside heavy nuclei (plural-multiple production).

S. A. Azimov and V. F. Višnevskij: **On the decay particles producing showers of nucleons and electrons.**

The authors have performed a series of measurements at Pamir at different altitudes (3 900 and 950 m) during the years 1950-51.

Transition for showers generated in water, and absorption mean free paths in water and in air have been studied.

The absorption mean free path in water results:

$$\lambda_a^{(H_2O)} = 223 \pm 15 \text{ g}\cdot\text{cm}^{-2}$$

and in air (measured between 950 and 3 900 m):

$$\lambda_a^{(air)} = 123 \pm 6 \text{ g}\cdot\text{cm}^{-2}\,.$$

From the analysis of results the authors conclude that about one third of shower-producing secondary particles decay in air (at average mountain altitudes).

M. I. Dajon: **Protons and mesons produced by cosmic rays neutrons.**

The author studied by means of a magnetic field of 6 200 gauss with the arrangement shown in fig. 24, the particles produced in a lead screen 9 cm thick.

The experiment has been conducted at the altitude of 3 250 m. In fig. 25 the spectrum of particles with range

$R \leqslant 8$ cm $C + 1$ cm Cu

is reproduced. The black portion refers to particles produced in lead by neutral incident particles. The author deduces, among other conclusions, that mainly negative mesons are produced in lead by neutrons.

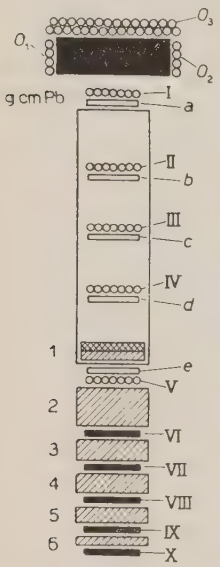


Fig. 24. — Arrangement with magnetic spectrometer (1-6 are filters of Cu, Al, C).

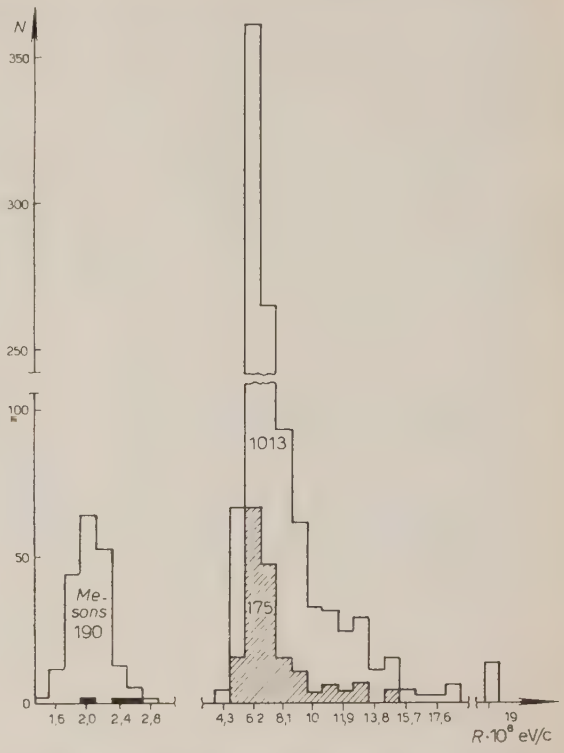


Fig. 25. — Spectrum of particles having a residual range $R = 8$ cm $C + 1$ cm Cu (blacked out areas refer to particles produced in Pb).

A. I. Alihanjan and G. A. Marikjan: **On fast deuterons in Cosmic Rays.**

Two sets of measurements have been performed in 1950-51 with the new magnetic spectrometer at Mount Alagez, one with a field of 6 200 gauss, the other with 14 000 gauss.

A group of particles with mass in the range 3500-4000 (deuterons) has been separated from the proton peak. The number of deuterons having a range from 3 to 6 cm in lead (200-400 MeV) results to be about 10% of the protons with equal range.

At least 25% of the recorded deuterons were produced in lead by incident neutrons. An approximate evaluation of the production cross-section, for neutrons having $E > 500$ MeV, gives $\sigma \sim 0.26\sigma_0$, where σ_0 is the geometrical cross-section of a lead nucleus.

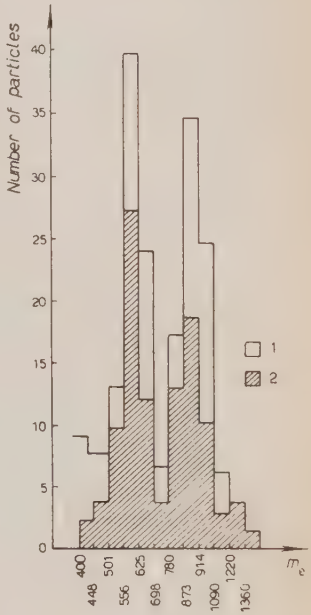


Fig. 26. Histogram of observed particles (· and) in function of masses.

G. B. ŽDANOV: **New elementary particles in the cosmic radiation.**

The author gives a detailed report on the works and results done outside the Soviet Union, which lead to the discovery of π-mesons, K particles and V particles.

He mentions also some results obtained recently by A. I. ALIHANJAN and coworkers with a new magnetic spectrometer (for particles having masses in the interval 400÷1400 m). Results are given in the fig. 26.

The author adds that these preliminary results are waiting for confirmation by other methods of observation.

V. M. HARITONOV: **Analysis of the ionising power of relativistic particles.**

The author reports on some measurements of ionising power as a function of momentum performed with the big magnetic spectrometer placed at the altitude of 3200 m on the Caucasus.

The results are in good agreement with the well known Landau formula (*), and show that for relativistic particles the ionization increases as a consequence of the density effect calculated by FERMI and WICK.

(*) L. LANDAU: *Journ. of Phys. USSR.* 8, 201 (1944).

G. A. Šajn and V. F. Gaze: **On a magnetic property of some gaseous nebulae.**

According to the authors the assumption that magnetic fields of the order of 10^{-5} gauss exist in the interstellar space of our Galaxy meets some objections.

The authors show that some indications exist about magneto-hydrodynamic processes in some nebulae which could be assumed as exemples of the magnetic fields postulated in Fermi's theory.

A. A. Logunov and J. P. Terleckij: **On the energy spectrum of primary cosmic ray particles.**

The authors start from the assumption that primary particles are emitted from the stars, then accelerated by induced electric field and finally further accelerated according to Fermi's mechanism in collision with moving magnetic fields in the Galaxy.

The authors intend to improve the results of Fermi's theory by treating more accurately the equations for the « turbolent » motion of magnetic fields. The integration of the equations, based on the assumption that the diffusion coefficient of the particle is proportional to its energy, leads to an energy spectrum of primary particles of the form:

$$f(E) \sim \beta \cdot E^{-2,5} \exp\left(-\frac{\beta}{\alpha} E\right)$$

in good agreement with experimental results (the effect of the exponential factor is negligible up to energies $\sim 10^{20}$ eV).

E. S. Glokova: **Variation of the meson component intensity during a cycle of solar activity.**

The author examines the well known measurements performed in the years 1937-46 in some stations where the cosmic radiation intensity is continuously recorded, particularly at Huankayo (Perù) and Cheltenham (U.S.A.).

The increase of the meson component intensity corresponding to an average decrease of solar activity is discussed in detail.

Recent Russian Work on Liquid Helium.

J. WILKS

The Clarendon Laboratory - Oxford, England

(ricevuto il 18 Giugno 1953)

CONTENTS

1. Introduction. – 2. Landau's Theory. 1. Elementary Excitations. 2. The two Densities. 3. Superfluidity. 4. Heat Flow in Helium. – **3. The Measurement of ϱ_n.** 1. Oscillation Experiments. 2. Rotation Experiments. **4. Second Sound.** 1. Velocity Measurements. 2. Critical Velocities. 3. Decay Measurements. 4. Shock Waves. – **5. Heat Transport.** 1. Heat Flow in Slits and Capillaries. 2. The Momentum of Heat Flow. 3. The Thermal Resistance of the Boundary Layer. – **6. Theory of Excitations.** 1. The Viscosity. 2. The Absorption of Sound. 3. Discussion. 4. Recent Developments. – **7. Landau's Theory below 1 °K.** 1. The Velocity of Second Sound. 2. Heat Flow. 3. The Two Fluid Model. – **8. The He II Film. – 9. The Critical Velocity. – 10. Solutions of ^{3}He in ^{4}He.** 1. Experimental. 2. Theoretical. – **11. The Properties of Pure ^{3}He.** 1. ^{3}He and ^{4}He. 2. ^{3}He. – **12. Feynman's Theory** (*). – 13. **Acknowledgements. 14. Bibliography.**

1. – Introduction.

Owing to the influence of Kapica's experiments on superfluidity and of Landau's theory — both published in 1941 — the Russian work on liquid helium forms a remarkably coherent whole. Nearly all the subsequent papers are concerned with working out the possibilities opened up by LANDAU; they therefore constitute a natural subject for review (**). Although of course some

(*) Added in proof.

(**) ANDRONIKAŠVILI [1] has given an interesting review, from the Russian point of view, of work done before 1949.

articles are of more consequence than others, I have attempted to refer to all the Russian contributions on liquid helium since 1940. On the other hand, reference is only made to authors outside Russia if it is really necessary for the discussion.

2. – Landau's Theory (*).

2·1. – *Elementary Excitations.*

LANDAU [3] considers that liquid helium II exists at so low a temperature that it is a « quantum liquid » whose thermal motion can be regarded as an aggregate of single « elementary excitations ». It is the essence of his theory that these are excitations of the whole liquid and not of individual atoms. LANDAU [4] states that it follows unambiguously from quantum mechanics that every slightly excited macroscopic system can be described in terms of « elementary excitations » which describe the « collective » motion of the particles and which have certain energies and momenta. As the liquid can transmit sound waves some of these excitations must be quanta of sound waves, or phonons, with the usual energy spectrum

$$\varepsilon = cp \,, \tag{1}$$

where ε and p are the energy and momentum of the excitation and c is the velocity of sound. Besides sound waves, LANDAU supposes that vortex motions will also contribute to the thermal energy and he develops a quantum hydrodynamics to determine the form of their energy spectrum. He gives a formalism for quantizing the motion of a fluid in terms of its density ϱ and velocity v, and claims to show that rot v (i.e., curl v) commutes with the Hamiltonian provided that over the whole liquid rot $v = 0$; hence the liquid has stationary states free of vortex motion. Moreover, by an analogy with angular momentum, LANDAU claims that the energy of the lowest excitation for vortex motion cannot be arbitrarily close to that of the lowest (non-vortex) state. There must be an energy gap Δ between the lowest vortex and non-vortex states; thus the spectrum for vortex excitations, or rotons, was taken to be

$$\varepsilon = \Delta + \frac{p^2}{2\mu} \,. \tag{2}$$

(*) For a more detailed discussion see the excellent review by DINGLE [2].

However after examining PEŠKOV's measurements on second sound (see § 4·1) LANDAU [5] concluded that better agreement was obtained by taking

$$\varepsilon = \Delta + \frac{(p - p_0)^2}{2\mu} . \tag{3}$$

The constants in these equations cannot be found theoretically and are deduced by postulating that, if the number of phonons and rotons is not too large, their interactions may be neglected and an assembly of them may be regarded as a mixture of two ideal gases — a phonon gas and a roton gas. Hence by using standard statistical methods the specific heat is evaluated in terms of the elementary excitations; the required constants may then be found by comparing this result with the measured values.

LANDAU's demonstration of the reality of these elementary excitations [3] is by no means rigorous and has often been criticised (e.g., LONDON [6], DINGLE [2]). Indeed until recently it seemed that the concepts of phonons and rotons were only justified by the success of Landau's theory. However KRONIG and THELLUNG [7] now claim to have given a rigorous proof of the existence of phonons while ZIMAN [8] using similar methods has demonstrated the possibility of a roton type spectrum of the form $\varepsilon = \Delta + p^2/2\mu$ (see also THELLUNG [9]). Both ZIMAN and THELLUNG mention that there will be interactions between rotons but do not discuss the validity of LANDAU's assumption that these may be ignored below about 1.8 °K where the roton-phonon gas is not too dense.

2·2. – *The Two Densities.*

LANDAU [3] now considers how the excitations manifest themselves. He postulates that the energy E and angular momentum M of a rotating vessel of helium are determined solely by the number and nature of the excitations. M is then evaluated by a statistical method; at absolute zero, where there are neither phonons nor rotons, $M = 0$. As the temperature is increased the value of M rises but is less than would be obtained by calculating M in the usual way. Thus it is as if only a fraction of the mass of helium rotates; this fraction is written as ϱ_n/ϱ where ϱ is the ordinary density and ϱ_n is a new parameter with the dimensions of density. By the law of mass conservation, the fraction of the mass which does not rotate is equal to $(\varrho - \varrho_n)/\varrho$ generally written ϱ_s/ϱ. The parameters ϱ_n and ϱ_s are known as the densities of the « normal » and « superfluid », but this nomenclature is unfortunate as the theory does not postulate any division of the helium into two real fluids; each density is associated with the whole volume of the helium. Nevertheless it is convenient to refer to the mass which does not take part in the motion as the superfluid and the rest (associated with the excitations) as normal fluid.

To obtain exact expressions for the value of ϱ_n, LANDAU calculates the momentum per unit volume associated with the excitations in the analogous but mathematically simpler case of a vessel of liquid helium moving with constant linear velocity V. This quantity, say $\mathbf{\Gamma}$, is just the aggregate of the momenta of the individual excitations and is found by summing them subject to the appropriate statistics. Hence ϱ_n is obtained by equating $\mathbf{\Gamma}$ with $\varrho_n V$; values derived in this way are in fairly good agreement with measurements by ANDRONIKAŠVILI and PEŠKOV (see § 3·1 and 4·1). Above about 1·8 °K however the theoretical values of ϱ_n/ϱ rise too slowly, so that the λ-point defined by $\varrho_n = \varrho$ is not reached until about 2.4 °K; this divergence is presumably due to the roton-phonon gas becoming so dense that the interaction terms can no longer be ignored.

2·3. – *Superfluidity.*

LANDAU concludes from the above picture that helium is superfluid. Suppose a liquid is flowing through a capillary tube with velocity V and is observed from a co-ordinate system in which the liquid is at rest and the tube moving. In general if the liquid has any viscosity the moving capillary will transfer momentum and energy to it, but in the case of helium, relations (1) (2) or (3) must always be satisfied. Considerations of conservation of energy and momentum lead directly to the condition that momentum cannot be transferred to helium at absolute zero in this way unless

$$(4) \qquad \begin{cases} V > c & \text{(phonons)} \\ V > \sqrt{\dfrac{2\Delta}{\mu}} & \text{(rotons)} . \end{cases}$$

Hence unless the velocity exceeds these values there is a complete absence of viscosity.

We now consider temperatures above absolute zero. As before, new excitations will not be created unless the critical velocities given by (4) are exceeded, but momentum can now be transferred — at all velocities — from the capillary to the thermal excitations which exist in the helium. Thus the excitations, or normal fluid, have a viscosity, η_n, which retards their flow through the tube. (It is also this viscosity which is responsible for the damping of a disc oscillating in liquid helium). However, by a similar argument to that used above, momentum can still not be transferred to the superfluid either from the capillary or from the excitations (*) unless the critical velocities are

(*) LANDAU does not discuss this latter essential qualification in any detail, see however LANDAU and POMERANČUK [81].

exceeded. Thus the superfluid part of the helium flows through the tube as if it had zero viscosity: for experimental details of such flow see, for example, KAPICA [37].

The values of the «critical» velocities derived from equations (4) are $2 \cdot 10^1$ and $6 \cdot 10^3$ cm/s for phonons and rotons respectively; these figures are larger than those determined experimentally by a factor of about 10^3. There is no satisfactory explanation of this discrepancy although GINZBURG [10] has put forward a tentative theory. (See § 9). The only other Russian discussion of superfluidity consists of an inconclusive paper by GEJLIKMAN [11] who adds little to LANDAU's treatment.

LANDAU [3] also postulated that the superfluidity is responsible for the formation of the mobile helium film: all liquids wetting a hard surface form a film, but generally this happens extremely slowly because of their viscosity. In the case of helium however he suggested that both formation and movement take place quickly due to the superfluid flow.

2·4. – *Heat Flow in Helium.*

LANDAU considers that since the entropy of the helium is entirely determined by the excitations, the motion of the superfluid cannot transfer heat and should therefore be thermodynamically reversible. Thus the fountain effect in capillaries sufficiently narrow to permit only the flow of superfluid should be a reversible phenomenon, and on this basis a thermodynamic proof is given of the LONDON [12] equation $\Delta P/\Delta T = \varrho S$.

The large heat conductivity observed in capillaries is explained by a relative motion of the two fluids, one carrying entropy, the other not. Here again LANDAU emphasises that rather than two fluids there are «two movements which take place simultaneously in one and the same liquid; one of these movements carries heat, the other does not». In order to treat heat flow in more detail, equations of motion for the two fluids are developed. Besides relations expressing the conservation of energy and momentum and the usual acceleration equation for a liquid, there is an additional acceleration equation for the superfluid deduced by a thermodynamic argument:

$$\frac{\partial v_s}{\partial t} + \nabla \Phi = 0 \,, \tag{5}$$

where Φ is the thermodynamic potential. By ignoring terms quadratic in the velocity in these equations of motion and by remembering that the thermal expansion coefficient of helium is so small that the adiabatic and isothermal compressibilities are nearly equal, it is possible to derive the velocity of sound. Actually two velocities c_1 and c_2 corresponding to two modes of motion are

found: $c_1^2 = \partial P/\partial \varrho$ and $c_2^2 = TS^2\varrho_s/C\varrho_n$, where S and C are the entropy and specific heat of the liquid.

The solutions of the equations of motion were subsequently shown by LANDAU [13] to be separable into two independent parts; one solution corresponds to a potential flow of superfluid while the other concerns only the normal fluid and is identical with the solutions of the Navier-Stokes equation for a liquid of density ϱ_n and viscosity η_n. Other authors outside Russia have derived equations of motion which differ from those of LANDAU in the second order terms, but their work has been criticised by DINGLE [2]. HALATNIKOV [87], however, has recently given hydrodynamical equations which, he claims, are formally valid for any values of the normal and superfluid velocities.

3. – The Measurement of ϱ_n.

3·1. – *Oscillation Experiments.*

The first comparatively direct measurement of the parameter ϱ_n was by ANDRONIKAŠVILI [14] who mounted fifty very thin discs close together (0.2 mm separation) on a common axis and observed their period of oscillation in liquid helium as a function of temperature. The periods of oscillation were such that one would have expected all the helium between the discs to be dragged round with them by viscous forces. In fact the moment of inertia of the oscillating system appeared to vary with temperature, and this was taken to be an indication that only a fraction, ϱ_n/ϱ, of the total mass of the helium was set in rotation. ANDRONIKAŠVILI's values for ϱ_n/ϱ are shown in fig. 1. ANDRONIKAŠVILI [15] also made experiments with one comparatively heavy disc so that the mass of helium dragged round was only a small correction term, and by measuring the damping in the usual way determined the quantity $\varrho_n\eta_n$, where η_n is the viscosity of the normal fluid.

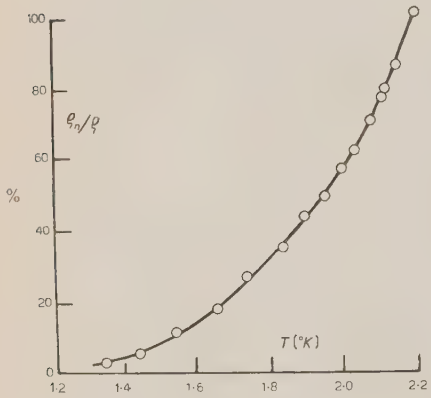


Fig. 1.

These Russian experiments have been repeated by HOLLIS-HALLETT [16] who obtains results within about 10% of those of ANDRONIKAŠVILI. (HOLLIS-HALLETT also gives a fuller mathematical treatment). The discrepancies are

easily accounted for by the difficulty in determining the dimensions of the apparatus and applying the various end corrections. Below about 1.5 °K, ϱ_n becomes very small but the absolute accuracy of the measurements remains unchanged and it becomes difficult to obtain reliable quantitative information. This is unfortunate, because although more accurate values of ϱ_n can be obtained from experiments on second sound (see § **4**), it would be valuable to have alternative means of deriving this important parameter. HOLLIS-HALLETT also made measurements on oscillations of greater amplitude and found that the decrement was no longer independent of the amplitude, as at lower amplitudes, probably because of the breakdown of perfect superfluidity. No Russians have done work on these lines as they appear to consider it more profitable to concentrate on the region of small velocities, thereby avoiding complicated transition effects.

3·2. – *Rotation Experiments.*

The agreement between the values of ϱ_n obtained from the oscillating disc experiment and those from the velocity of second sound and from Landau's theory is sufficient justification for the introduction of this new parameter. Nevertheless one would welcome a measurement of ϱ_n based directly on Landau's definition and not involving the viscosity of the normal component. For instance, the moment of inertia of a rotating cylinder of helium can in principle be found by measuring the work done in accelerating a vessel of the liquid to a constant velocity. The experimental difficulties are considerable but an ingeneous experiment on these lines has been made by ANDRONIKAŠVILI [17] following an earlier discussion by PIPPARD and MOTT [18]. A cylindrical vessel in which are fixed closely spaced discs is filled with helium and rotated slowly on a torsion suspension at a temperature just *below* the λ-point; it is then cooled to 1.5 °K and brought smoothly to rest. The normal fluid will come to rest with the discs but if the superfluid is rotating, as might perhaps be expected, it will continue to rotate. The temperature of the helium is then suddenly raised to 1.65 °K thus destroying 10 % of the superfluid which comes to rest as normal fluid; hence by the conservation of angular momentum a considerable angular deflection of the vessel should be observed. (ANDRONIKAŠVILI assumes conservation of energy — this is probably an error). No appreciable deflection was however observed and the conclusion was drawn that there are no « persistent currents » in liquid helium. On Landau's theory [3] this negative result is not altogether surprising; the superfluid will not take part in the rotation, and therefore at 1.5 °K both normal and superfluid components are at rest. This result however implies that if the vessel were rotated steadily at 1.5 °K and suddenly cooled, then there should be an acceleration

of the vessel as normal fluid becomes superfluid at rest. Such an experiment would of course present technical difficulties.

4. – Second Sound.

4·1. – *Velocity Measurements.*

The earliest prediction of temperature waves in liquid helium is due to TISZA [19], but at the time of writing his first paper LANDAU was apparently unaware of this work and seems to have thought that the second velocity of sound c_2 which he predicted would be associated with sound of the usual type. It was only after Peškov's failure to excite second sound with a piezo-electric generator [20] that LIFŠIC [21] showed that an oscillating plate radiates second sound about 10^6 times less intensely than first sound, but that a plate with a periodically varying temperature would excite temperature waves of second sound almost exclusively. PEŠKOV [22, 20] after detecting such waves measured their velocity at temperatures down to 1.2 °K and deduced values of ϱ_n in good agreement with those of ANDRONIKAŠVILI and in fair agreement with LANDAU's first paper. PEŠKOV's results were first confirmed by FAIRBANK, FAIRBANK and LANE [23], and later by other workers. At the lower temperatures, however, the velocity fell slightly with temperature; in particular there was no sign of the velocity rising towards the predicted value of $c/\sqrt{3}$ at absolute zero. From a study of PEŠKOV's results LANDAU [5] deduced that the energy spectrum for rotons should be of the form already mentioned (4); this spectrum leads to a slight minimum in the velocity at about 1.1 °K before it rises at lower temperatures to the value $c/\sqrt{3}$. PEŠKOV [24] then extended his measurements and observed the velocity increasing from 1.1 °K to 1.0 °K. Subsequent work outside Russia has fully confirmed these measurements and extended them to much lower temperatures where velocities of about $c/\sqrt{3}$ are observed (see § **7**). PEŠKOV himself has made measurements down to 0.85 °K [25], has shown that there is no velocity dispersion down to 10 Hz [26], and has measured the velocity as a function of pressure [27].

4·2. – *Critical Velocities.*

Nearly all the phenomena concerning liquid helium in slits or capillaries are characterised by a change in behaviour when the velocity of the normal or superfluid reaches the order of about 10 cm/s. PEŠKOV [28] observes that some of his measurements on second sound at 2.05 °K involved normal and superfluid velocities of 20 and 50 cm/s respectively, but no « discontinuities »

were observed; hence if there are critical velocities associated with second sound their values are still higher. Although nearly all the observations on critical velocities have been made in slits it would be surprising if similar effects vere not observed in the bulk liquid, particularly as the critical velocity seems to be roughly inversely proportional to the width of the slit. Moreover the only relevant data on bulk liquid — HOLLIS-HALLETT's observations on a disc oscillating in liquid helium [17] — show the presence of critical velocity effects. Clearly it is desirable to investigate second sound of greater amplitude corresponding to larger velocities of the «fluids» but it is difficult to put in sufficient power without causing the helium around the heater to vaporize.

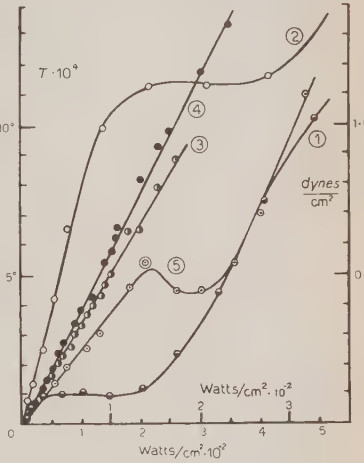


Fig. 2.

Although unable to produce very high velocities of the two fluids by the thermal excitation of second sound, PEŠKOV studied the amplitude of these waves as a function of heat input and his results are shown in fig. 2. Curve 1 is for a frequency of 200 Hz at $T = 1.63$ °K and curve 2 is for similar conditions save that the helium is under 20 atmospheres pressure. In curve 1 there is a plateau corresponding to values of v_n of about 1 to 5 cm/s which suggests that the critical velocity has been exceeded; if so however it is somewhat surprising that the curve rises again with higher heat inputs. PEŠKOV points out that this behaviour is reminiscent of observations by KAPICA who measured the pressure due to the momentum of heat flow in helium as a function of the heat flow. (See § 5·2). Curve 5 shows these results, the upper scale of abscissae and the right-hand scale of ordinates refer to this diagram; the value of v_n at the plateau is about 20 cm/s.

PEŠKOV [28] also excited second sound by a filtration method; the generator consists of a small box one side of which is made of a copper filter with holes sufficiently fine to pass only superfluid. The opposite side of the box is a steel membrane which is vibrated so as to force superfluid through the filter and thus set up waves of second sound. Of course this method also excites first sound, but PEŠKOV [29] has shown that second sound predominates; in any case the resonances due to the two sounds can be detected separately. (It also has the advantage that no net heating is produced). Using this method to produce waves of similar amplitude as before PEŠKOV obtained curves 3 and 4 ($T = 1.63$ °K, 200 Hz and 700 Hz); as the amplitude now increases

steadily with heat input, the plateau seems to be associated with excitation by heating.

4·3. – *Decay Measurements.*

Peškov [28] has investigated the energy losses responsible for the decay of second sound by measuring the half widths of resonance curves. As the losses appear to vary as the square root rather than as the square of the frequency they are assumed to be mainly due to an out of phase heat transfer to the walls of the vessel containing the helium. Peškov [29] and Dingle [30] have obtained differing expressions for the magnitude of the surface losses; and both treatments have been criticised by Halatnikov [31] who repeats Peškov's calculations taking into account the temperature jump at the boundary of helium II with a solid. (See § 5·3).

4·4. – *Shock Waves.*

If large amplitude pulses of sound are propagated in a liquid, the second order terms in the equations of motion are responsible for the formation of shock waves. Such shock waves of second sound have been observed by Osborne [32]: below 1.96 °K the leading edge of the pulse is steepened as for shock waves in normal liquids, while between 1.96 °K and the λ-point the back edge is steepened. A theoretical treatment has been given by Temperley [33] but has been criticised by Halatnikov [34, 35] on the grounds that his equations of motion are incorrect. Starting from Landau's equations of motion Halatnikov arrives at similar results to Temperley's for the higher temperatures and explicitly predicts that between 0.5 and 0.9 °K the shock front will again appear at the rear of the pulse, as above 1.96 °K. For first sound he deduces that the shock appears on the leading edge provided $\partial/\partial\varrho\cdot(\varrho c_1)$ is positive; c_1 is the velocity of ordinary sound and this condition is always satisfied. For second sound the shock appears on the front or back edge of the pulse according as $\partial/\partial T\cdot\ln(c_2^3\cdot C/T)$ is positive or negative; the predictions mentioned above follow immediately from the temperature dependence of c_2.

5. – Heat Transport.

5·1. – *Heat Flow in Slits and Capillaries.*

Landau's theory has been applied to heat flow by Andronikašvili [36] who considers the relative motion of the two « fluids » in a capillary with a temperature difference ΔT across its ends. The normal fluid flows from the hot to the cold end, and superfluid from the cold to the hot; the process is

limited by the rate at which the fountain pressure ΔP (associated with ΔT) can drive the normal fluid through the tube. ANDRONIKAŠVILI takes

$$v_n = w/\varrho Q \quad \text{and} \quad \Delta P = \varrho Q \Delta T/T ,$$

where w is the heat current density and Q is what is termed the heat content of helium. (There is some confusion in the Russian nomenclature for Q. Although Q in the LONDON [12] equation is really the heat of transport, KAPICA [37] refers to it as the heat content and then sets it equal to TS which is certainly not the enthalpy. Here we assume with LONDON, Q TS). Using the above two equations together with Poiseuille's equation for the viscous flow of the normal fluid, one finds for a flat slit of perimeter R, width d and length Δx that the total heat flow W is given by

$$W = \frac{R \cdot d^3 \cdot \varrho^2 \cdot Q^2}{12 \eta_n \cdot T} \frac{\Delta T}{\Delta x} . \tag{6}$$

This result had previously been obtained by LONDON and ZILSEL [38] in a stightly different way.

MELLINK [39] has made measurements on slits of width 5 μ and 10 μ and has observed such a linear relation between W and ΔT for small heat flows, corresponding to relative velocities between normal and superfluids of not more than about 20 cm/s. Bearing in mind that W depends very critically on the width of the slit which is difficult to measure accurately, there is quite good agreement with equation (6). It is noteworthy that for sufficiently small heat flows the apparent conductivity increases steadily up to the λ-point. When the critical velocities are exceeded, either by increasing ΔT or by working in wider capillaries, the problem becomes much more complicated and there is no Russian treatment. ANDRONIKAŠVILI does however criticise Gorter's [40] interpretation of Mellink's results for higher heat flows.

ANDRONIKAŠVILI gives a fair account of small heat flows in not too large slits; however in slits smaller than 5 μ the heat flow is greater than is given by (6). As is discussed below (§ 6·1) the mean free path characterising the viscosity of the normal fluid is of the order of 1 μ at 1.6 °K and increases with falling temperature; thus some divergence from equation (6) is to be expected in small capillaries. Although the general effect of approaching the Knudsen region will be to reduce the apparent viscosity, the observed values of heat flow in very narrow slits seem too large for this explanation alone to be sufficient.

5·2. – *The Momentum of Heat Flow.*

The momentum associated with heat flow in helium was first observed by KAPICA [41] who immersed in the liquid a bulb to which was attached a

capillary tube, both bulb and capillary being thermally insulated by a vacuum jacket. On supplying heat to the bulb there was apparently a flow of liquid out of the capillary in the form of a well defined jet, which would deflect a vane suspended on a torsion wire. KAPICA was able to measure the force on the vane as a function of temperature and of heat input to the bulb. On Landau's theory the jet consists of normal fluid flowing away from the heat source with a momentum equal to

$$\varrho_n w/\varrho S T\,, \tag{7}$$

where w is the heat supplied per second and S in the entropy. PEŠKOV [26] has observed however that Kapica's values for the force on the vane are only about half those to be expected from this relation. (Although PEŠKOV does not say so explicitly, the discrepancy is even more serious as KAPICA observed a force proportional to w whereas expression (7) leads to a force proportional to w^2 (*)). As steady heating may be regarded as the excitation of second sound of zero frequency, PEŠKOV investigated whether this result of Kapica's was reflected in a dispersion of second sound at low frequencies. He found no dispersion in the range 10–250 Hz. Taking this with the very indirect evidence that values of ϱ_n deduced from ANDRONIKAŠVILI's observations on discs oscillating at a frequency of 1/25 Hz agree with the values deduced from all the second sound measurements, he postulated that there is no such dispersion at all. Hence he concluded that either the apparently fundamental relation (7) is wrong or there was some error in Kapica's experiment. In view of the importance and apparent simplicity of the expression in question, the discrepancy seems worthy of further attention.

It is also convenient to mention here STRELKOV's radiometer [42] whose behaviour has never been satisfactorily explained. The radiometer consisted essentially of two vanes suspended on a torsion wire in liquid helium; on heating the vanes by shining a light on them a torque was observed. In liquid helium I the direction of the torque is such that the vanes move towards the light source, as in the case of other liquids and dense gases. However, at the λ-point the direction of the torque changes and below the λ-point the vanes move away from the light as happens in a rarefied gas. Rough quantitative measurements showed that the torque below the λ-point increases approximately linearly with decreasing temperature down to 1.7 °K: no further work has been reported. STRELKOV [43] has also described the construction of an ingenious « optical » dewar whereby it is possible to look directly at liquid helium by way of optical flats only. Using this dewar he tried to detect

(*) I am indebted to Mr. H. E. HALL for drawing my attention to this point.

changes in the optical properties of liquid helium II due to a heating element immersed in it; no disturbances were observed until the liquid vaporized. Finally we mention that Savić and Šal'nikov [44] observed a fine colloidal suspension of crystals of solid air in liquid helium I coagulate and precipitate as flakes when the temperature was lowered through the λ-point. Although this phenomenon is obviously associated with the different types of thermal excitations in helium I and II no explanation of the effect has been given.

5·3. – *The Thermal Resistance of the Boundary Layer.*

Kapica [41] attempted to measure the thermal conductivity of bulk liquid helium II by supplying heat to a resistance wire immersed in the liquid and observing the temperature rise in the wire. Although the heat flow away from the wire was very much greater in helium II than in helium I, it was also very much smaller in magnitude than the heat flows observed in capillaries. The temperature rise of the wire was linearly proportional to the heat input; the heat flow for a given temperature difference varied approximately as T^3, and there was no sign of any maximum in the heat flow below the λ-point. Kapica also gave an ingenious demonstration that virtually all the thermal resistance occurred in a thin layer of helium adjacent to the wire and no more than a few hundredths of a millimetre thick.

Landau [3] suggested that, as the heat flow in these experiments would be associated with normal fluid flowing from the heater and with superfluid flowing to it, the temperature jump in the surface layer was associated with the mechanism whereby superfluid was converted into normal fluid. Although various authors have given treatments based on such a phenomenological basis, the most promising approach is due to Halatnikov [31]. The essence of this author's work is that the large discrepancy between the acoustic impedances of liquid helium and ordinary solids makes it difficult for sound waves to pass from one to the other, (Pellam and Squire [45]). Hence in order to obtain an appreciable transfer of heat there must be a finite temperature difference. Halatnikov gives a detailed treatment in which he calculates the energy radiated into liquid helium by a vibrating wall and concludes that the heat flow w is given by

$$w = AT^3 \cdot \Delta T \,. \tag{8}$$

The constant A is completely defined in terms of the elastic constants of the wall and the characteristic constants of helium; the T^3 term reflects the fact that the transfer of heat is essentially due to sound waves (phonons). As the heat transfer in liquid helium itself is very great the only temperature differ-

ence large enough to be observed is that at the interface, and the whole thermal resistance appears to be concentrated at the surface of the helium.

Although relation (8) is of the form observed by KAPICA, the temperature jump he observed was « several orders » less than is obtained by evaluating A. HALATNIKOV points out that if the surface of the wall is rough, or if « parasitic heat flows » occur, the heat transfer may be very much greater. Then again near the λ-point the modification of the vibrations of the wall due to the presence of the helium may become important; also the elastic constants of Kapica's surfaces are not known accurately at low temperatures. The position is still by no means clear and further work both experimental and theoretical seems desirable. For example, on this theory, the temperature jump between helium and a wall should depend very appreciably on the elastic constants of the wall; (Kapica's experiments where he placed films of oil on the surface are hard to interpret because the state of the oil after solidification is unknown). Moreover as HALATNIKOV considers only sound waves and not electronic excitations it would be desirable to work with dielectrics.

6. – Theory of Excitations.

LANDAU and HALATNIKOV have developed methods for deriving from Landau's theory the viscosity and the absorption coefficients for first and second sound. In their first papers [46, 47] these authors calculate the viscosity of the normal component of helium by postulating that for not too high temperatures (less than about 1.8 °K) the elementary excitations may be treated as an ideal gas of phonons and rotons. Thus, in the presence of a velocity gradient, momentum will be transferred by processes analogous to viscous processes in a real gas. An entirely rigorous treatment is probably impossible because of the complexity of the problem; there are several scattering processes to be considered and for each process the scattering parameter is a function of the energy of the particular phonons and rotons in question. Therefore LANDAU and HALATNIKOV make various simplifying assumptions which enable them to obtain solutions which though not entirely unambiguous are shown to be self consistent. We first consider their treatment of the viscosity of the normal component.

6·1. – *The Viscosity* η_n.

The mechanisms of the viscous processes are quite analogous to those considered in gas kinetic theory; mean free paths may be deduced for phonons and rotons such that the transfer of momentum is proportional to them. It

is also convenient to regard separately the momentum carried by phonons and by rotons, and to derive the viscosity as the sum of a phonon and a roton viscosity. The scattering parameter for the phonons is calculated by perturbation theory from their energy spectrum specified in terms of the basic constants in equation (1) and (3). (See § 6·3). Collisions between rotons are dealt with by taking their interaction energy to be a δ-function of the distance between them; for the interaction of phonons and rotons, the roton is treated as « some sort of particle in the phonon field ». Since rotons are comparatively « heavy » it turns out that their mean free paths are virtually always terminated by collisions with other rotons, and the associated viscosity η_R comes out to be temperature independent. (This result is quite analogous to the viscosity of a perfect gas being independent of its density). Owing to lack of data on rotons the numerical magnitude of η_R cannot be calculated.

The phonons have a very wide energy spread and may be scattered either by other phonons or by rotons, hence the calculation of the corresponding viscosity is more complex. However it is shown that above 1 °K the mean free paths of phonons are terminated almost entirely by collisions with rotons; these collisions are comparatively rare, so that in calculating the viscosity both the roton gas and the phonon gas may each be considered to be in internal equilibrium. The phonon viscosity is then calculated in terms of parameters derived from the velocities of first and second sound as functions of pressure. As the temperature falls this phonon viscosity increases rapidly — the number of rotons decreases exponentially with a consequent increase in the phonon mean free path. The difference between this phonon viscosity and the observed viscosity is temperature independent and is taken to be the roton viscosity. Although good agreement is obtained with the measured value of η_n, this is probably fortuitous both because of the necessarily approximate nature of the treatment and because the essential parameters are not known very accurately. Nevertheless the theory gives a reasonable account of the very considerable increase in η_n observed below 1.6 °K.

At lower temperatures the picture becomes more complicated. Above 1 °K, it is postulated that the only significant interactions between phonons are four phonon processes (i.e. two phonons collide and convert into two new phonons) in which all the phonons travel in approximately the same direction. These are the processes which are responsible for the equilibrium in the phonon gas to which we have already referred; as all the scattering is through very small angles however, the distribution function for the phonons is not given simply by the Planck function but by

$$n = (\exp[\alpha' \pm pc/kT'] - 1)^{-1}, \tag{9}$$

where α' and T' depend on the direction of the momentum of the phonons in

question. Below 0.8 °K however five phonon processes (i.e. two phonons collide and give rise to three, or vice versa) become much more frequent and it is they rather than four phonon processes which maintain the phonon equilibrium. Since this scattering is not confined to small angles, the equilibrium is now specified by a Planck function and the viscosity must be recalculated. The viscosity in the transition region is obtained by interpolation. Below 0.7 °K a further difficulty arises in that the number of rotons becomes so small that only phonon-phonon scattering is important; this region is not dealt with at all fully.

6·2. – *Absorption of Sound.*

HALATNIKOV [48] has also treated the attenuation of first and second sound by similar methods. In liquid helium the two specific heat C_p and C_v are so nearly equal that virtually all the attenuation will be due to viscous effects; it can also be shown that the usual expression for the attenuation of first sound in a liquid must be modified by replacing the usual coefficient of viscosity by η_n. However the attenuation predicted in this way is an order of magnitude too small and decreases with falling temperature, in contrast to the observations of PELLAM and SQUIRE [45] and of ATKINS and CHASE [49]. Discrepancies in magnitude are found quite commonly in liquids (see for example KARIM and ROSENHEAD [50]) and are explained by a « second » coefficient of viscosity associated with changes in volume unaccompanied by shear. HALATNIKOV assumes that helium II exhibits this second viscosity and relates it to relaxation effects associated with the changes in the number of phonons and rotons which must occur when the external parameters of the helium are varied.

It is assumed that the number of phonons may change as the result of five phonon processes and by the conversion of rotons to phonons (one roton two phonon processes), while the number of rotons changes as the result of roton-roton collisions or roton-phonon conversions. If the total number of phonons or rotons is not equal to the equilibrium value, the distribution function will contain chemical potentials μ_P and μ_R so that the rate of change of the number of excitations may be written:

$$\left\{\begin{array}{l} \dot{N}_P + \operatorname{div} N_P \cdot v_n = -\gamma_{PP}\mu_P + \gamma_{PR}\mu_R \,, \\ \dot{N}_R + \operatorname{div} N_R \cdot v_n = \quad \gamma_{RP}\mu_P - \gamma_{RR}\mu_R \,. \end{array}\right. \tag{10}$$

The γ's are kinetic coefficients (cf. LANDAU and LIFŠIC [51]) and HALATNIKOV obtains expressions for them by a consideration of the processes involved. It turns out that the effect of roton-roton collisions may be neglected: the temperature dependence of the coefficients associated with five phonon and

roton-phonon processes may be calculated but the numerical factors have to be deduced later from experimental data. The results of these calculations are expressed in terms of relaxation times θ_P, θ_R, and θ_{PR} characteristic of each process.

The present treatment is only valid for sound whose period is substantially greater than the relaxation times θ_P and θ_{PR}, for otherwise dispersion effects have to be considered. This condition is by no means negligible, for the viscosities are so small that high frequencies are necessary in order to observe any appreciable absorption; however it appears to have been satisfied by all the measurements to date. Values are also given of the velocity which would be observed at infinite frequency; the effect of dispersion is small and very high frequencies would have to be propagated in order to observe it. Finally values are given of the attenuation coefficients for first and second sound. The theory gives quite good agreement with PELLAM and SQUIRE's previous measurements on first sound after suitable values for the numerical coefficients referred to above are selected empirically. Although the presence of a second viscosity in helium II calls for no comment, it is remarkable that helium I in contrast to nearly all other liquids has no second viscosity; PELLAM and SQUIRE showed that the classical formula completely accounts for the absorption.

6·3. – *Discussion.*

At the time of their publication these papers gave a theoretical background to Andronikašvili's measurements of η_n, to Pellam and Squire's absorption measurements and to the fact that PEŠKOV had observed no dispersion of second sound. Several numerical coefficients had to be determined by appeal to experiments but the phonon component of the viscosity could be obtained unambiguously and gave the right answer. Although both η_n and the absorption coefficient of first sound have since been measured at slightly lower temperatures and increases in their magnitudes observed in agreement with the theories, these measurements would have to be extended to at least 0.8 °K to provide a check of real rigour.

Perhaps the least satisfactory part of these theories is that although the rotons play an essential role, very little is known about them. For instance, LANDAU in his 1941 paper postulates two distinct energy spectra for phonons and rotons (equations (1) and (2)), but when in 1947 he amended the roton spectrum to (3) he also said that there is really only one spectrum, with a phonon section for low values of the momenta and a roton section for high values. In general the phonon and roton sections are treated quite separately but the postulate that they are both parts of the same spectrum introduces the dispersion in the phonon spectrum which makes possible interactions

between phonons. (Phonons defined solely by $\varepsilon = pc$ would not interact with one another). Other points which have provoked criticism include the possibility of there being other relevant scattering processes; TEMPERLEY [52] for example, suggests that three phonon processes may be important. However, LANDAU and HALATNIKOV have at least given a reasonable explanation of the behaviour of η_n and the absorption coefficient — so far the only one. Moreover if the basic concepts of these authors are correct, the problem of working out detailed properties will always be very involved.

6·4. – *Recent Developments.*

HALATNIKOV [53, 54] has subsequently given a more detailed treatment of the absorption of sound starting from a form of the Boltzmann equation for excitations defined quite generally by the energy spectrum $\varepsilon = f(p)$. He solves this equation taking into account the motion of the superfluid and shows, that besides the kinetic coefficients mentioned in his earlier paper, there is also another coefficient analogous to that of thermal conductivity in ordinary substances. The effect of this new coefficient on the values previously obtained for the absorption of first sound is small, but it is responsible for a considerable increase in the predicted values of the absorption of second sound. Although very recent measurements [113, 114] appear to confirm this treatment, it seems to the writer that nearly all HALATNIKOV's work on this subject (including his recent treatment of ^{3}He - ^{4}He solutions) is open to some quite general criticism. For example, in spite of long and tedious mathematics, some of the essential parameters turn out to be so complex that their numerical values can only be found by appeal to experiment. The real question however is whether such a heavy mathematical superstructure is justified on the doubtful foundations of the phonon and roton spectrums which are at best only an approximation. For instance Landau's decision to change from roton spectrum (2) to (3) was somewhat intuitive and the Russian use of a similar roton type spectrum for ^{3}He *atoms* is even more obscure. (See § 10·2). In view of KRONIG and THELLUNG's work on phonons [7] it would seem that at present the best hope of arriving at a more rigorous treatment would be by concentrating on the region below 0.6 °K. Unfortunately, as we discuss in the next paragraph, the great length of the mean free path of phonons in this region introduces further complications.

7. – Landau's Theory below 1 °K.

7·1. – *The Velocity of Second Sound.*

LANDAU's predictions concerning the velocity of second sound below 1.0 °K have rightly been regarded as a crucial test to differentiate between

his theory and that of TISZA [55]. LANDAU takes the normal fluid to be associated with all the quantum *excitations* of the liquid, that is with the phonons and rotons, and hence deduces an increase in velocity as the temperature falls below 1.0 °K. TISZA on the other hand seems to have thought of the normal fluid as consisting of *atoms* (or gas-like *molecules*) and by a different argument concluded that the velocity should fall steadily to zero.

The agreement between Landau's theory and experiment is seen to be good in the region where many of the excitations are rotons. Measurements by both pulse and by standing wave methods (PEŠKOV [25]) clearly show that between 1.0 and 0.85 °K there is a considerable rise in the velocity of second sound. Below about 0.6 °K LANDAU predicted, in agreement with subsequent specific heat measurements [56], that the thermal excitations would all be phonons and a velocity of $c/\sqrt{3}$ might be expected. Although the original work of ATKINS and OSBORNE [57] in this region, using a pulse technique, has been repeated by several authors (e.g. [58, 59]) the experimental evidence is still somewhat obscure as the received pulse becomes very broad at the lower temperatures (*).

Possibly the observed phenomenon may be a type of thermal diffusion (GORTER [60]); this would not however be necessarily inconsistent with Landau's theory (see for example ATKINS [62]). At lower temperatures the mean free path of the phonons becomes comparable in size with the dimensions of the container and with the wavelength of the second sound (LANDAU and HALATNIKOV [47]); thus the phonons associated with a heat pulse may diffuse down the helium bath like atoms in a Knudsen gas. (This would be very similar to the diffusion of phonons in a dielectric whose thermal conductivity is limited by boundary scattering). On this picture, the shape of the pulse and its apparent velocity will depend on the size and shape of the bath of helium. As yet, there is little experimental data on this point, but ZIMAN [61] has shown that Atkins and Osborne's results are not inconsistent with this interpretation. Finally, we may note that if the mean free path of the phonons is limited by the container, then the viscosity η_n will eventually fall as the temperature approaches zero; however, in this region the product $\varrho_n \eta_n$ will be so small that it will be very difficult to observe any viscous effects at all.

7·2. – *Heat Flow.*

Although the question of heat transport in helium below 1 °K is a very interesting one, not much data is available. Following ANDRONIKAŠVILI's

(*) If, however, a small concentration of ^{3}He is present in the ^{4}He, undistorted pulses are observed down to 0.2 °K (KING and FAIRBANK [86]).

treatment of heat flow in capillaries (see § 5) we find that below about 0.6 °K the contribution to the heat flow by relative motion of the two « fluids » will be very small — this comes about principally because of the term Q^2 in equation (6). KURTI and SIMON [63] have measured the thermal *resistance* of a capillary of liquid helium below 0.5 °K and found values which are actually greater than those observed in solid helium at the same temperatures [64]. (KURTI and SIMON's results must be used with caution as their values include the thermal resistance between the helium and paramagnetic salts at the ends of the capillary; however the areas of contact between the helium and the powdered salt were very considerable).

7·3. – *The Two Fluid Model.*

Finally we mention a somewhat different approach to the nature of second sound based on a remark by PEŠKOV [20] that second sound could be regarded as a « sound vibration in a gas of thermal quanta ». WARD and WILKS [65] subsequently showed that in the low temperature phonon region any disturbance in the phonon distribution function would (subject to certain conditions) be propagated as a wave motion with velocity $c/\sqrt{3}$. On this picture second sound is a variation of the phonon distribution propagated by phonon interaction of the type which do not give rise to destructive scattering. The interest of this approach to second sound lies in the fact that it does not postulate a two fluid model or indeed any conditions which are essentially characteristic of helium, and PEŠKOV has remarked that second sound might be expected in perfect crystals free of imperfections which would scatter the phonons. Work on dielectric crystals [66, 67] has since shown that it is possible by a suitable choice of crystal and temperature range (e.g. corundum or artificial sapphire at helium temperatures) to realize conditions in which the only destructive scattering is by the walls of the specimen. If there are then still sufficient interactions between the phonons, it should be possible to observe second sound. It would therefore be of interest to determine how pulses of heat are propagated in such crystals; unfortunately their low specific heat combined with a high velocity of sound call for the use of very narrow pulses which can only be observed by thermometers of extremely small thermal capacity. The experimental difficulties are considerable, indeed the most promising crystal to use would seem to be solid helium at temperatures well below 1 °K!

The above mentioned treatment applies only to the temperature region where the thermal excitations are phonons but attempts have been made to extend it to deal with all types of excitations. For example, DINGLE [68] has generalised the earlier work and obtained the relation $c_2^2 = TS^2\varrho/C\varrho_n$. At low temperatures this is a good approximation to Landau's formula, but

at higher temperatures ϱ/ϱ_n is quite different from ϱ_s/ϱ_n: it is instructive to see where this discrepancy arises. The point is that fluctuations in the gas of thermal quanta must be accompanied by corresponding changes in the pressure and density of the liquid helium itself. Poth DINGLE and WARD and WILKS ignore these changes, whereas LANDAU takes them into account in the following way. Although he deduces the normal density ϱ_n by a dynamical argument (see § 2·3) he implicitly assumes in his equations of motion that this quantity may be treated as an invariant inertial mass. Hence as a fluctuation of temperature is accompanied by a fluctuation in ϱ_n and as the ordinary density of the helium is assumed to remain constant, then the relation $\varrho_n + \varrho_s = \varrho$ implies a drift of superfluid mass to or from the temperature fluctuation. By taking into account this drift of superfluid LANDAU arrives at the usual expression $c_2^2 = TS^2\varrho_s/C\varrho_n$. However the assumption that ϱ_n may be treated as an invariant inertial mass is by no means obvious and requires further elucidation. (For an approach to this problem see KRAMERS [69]).

8. – The He II Film.

JESELSON and LAZAREV [70] have recently given a long account of their experiments on the rate of film flow into and out of beakers. Although they mention some details of interest, no significant new results are reported. KAGANOV and JESELSON [71] have criticised ATKINS' treatment of oscillations of the film [72], and have in turn been criticised by DINGLE [73]: the difficulty lies in choosing the correct equations of motion for the helium in the film.

9. – The Critical Velocity.

LANDAU [3] predicted a critical velocity of about $6 \cdot 10^3$ cm/s in contrast to the values deduced from experiments on slits and capillaries and from the damping of an oscillating disc, which are of the order of 10 cm/s. The experimental evidence suggests that all phenomena in the region where superfluidity breaks down are very complex but, even so, any satisfactory theory of the liquid must predict the critical velocity to an order of magnitude. LANDAU remarks that it is essential for the two « fluids » to be able to flow through one another without exciting frictional forces, but does not enlarge on this important and perhaps crucial point.

Although the failure to predict the correct critical velocity is one of the most serious criticisms of Landau's theory, there is no satisfactory treatment by other authors. The empirical relation observed in slits, $v_c d \sim 10^{-3}$ cm, can be interpreted in terms of the uncertainty principle (BIJL, DE BOER and MI-

CHELS [74]) but this treatment hardly applies to viscosity measurements on the bulk liquid. GORTER and MELLINK [75] have shown that a mutual friction between the two fluids can give quite a fair explanation of phenomena above the critical region, but it appears that in general the phenomena are too complicated to be classified in terms of only one parameter. At present the source of any mutual friction remains obscure and its magnitude can only be deduced a posteriori. (See however ZILSEL and FRIED [76]). The only Russian contribution on this subject is by GINZBURG [10] who suggests that Landau's relation for the roton spectrum should be replaced by $\varepsilon = p^2/2\mu$. Landau's arguments applied to this spectrum, which has no energy gap Δ, lead to a critical velocity zero. GINZBURG however shows that if the helium is in a narrow slit of width d the effect of the uncertainty principle is to increase the critical velocity to a value in rough agreement with the experimental relation $v_c d \sim 10^{-3}$. The postulated energy spectrum however is in contradiction to LANDAU's, and would not lead to the correct temperature dependence of the specific heat and ϱ_n: GINZBURG therefore suggests that excitations of the type $\varepsilon = p^2/2\mu$ may be a form of surface motion which though important in slits would have no effect on the thermodynamic properties of the bulk liquid. If this were so, ϱ_n might have different values in slits and in the bulk liquid; GINZBURG remarks that it would be interesting to measure ϱ_n in slits, but does not suggest a method.

10. – Solutions of ^{3}He in ^{4}He.

10·1. – *Experimental.*

JESELSON and LAZAREV [77] have obtained 1.5% solutions of ^{3}He in ^{4}He by a preliminary enrichment, depending on the thermomechanical effect, followed by a further enrichment in a thermal diffusion column. They have made several measurements on these solutions including determinations of the λ-point [78], the rate of film flow [78], and the vapour pressure [79]. In general their results are in fair agreement with those obtained by other workers who have had access to solutions containing much greater concentrations of ^{3}He. (See for example DAUNT [80]).

10·2. – *Theoretical.*

Recent work in America and Holland has shown that the properties of solutions of ^{3}He in ^{4}He and of pure ^{3}He are substantially different from those of pure ^{4}He. In considering the Russian work on this subject it must be

noted that their treatments of ^{3}He - ^{4}He solutions and pure ^{3}He are quite distinct.

The behaviour of ^{3}He - ^{4}He solutions was first considered by LANDAU and POMERANČUK [81] who gave a discussion applicable to solutions of any foreign atoms in helium II. It is assumed that the number of foreign atoms is small so that they interact only with the ^{4}He and not with one another. The energy spectrum of the solution consists of phonons and rotons plus additional levels associated with the solute. The foreign atoms are not to be regarded as localised in space but like electrons in metals move through the whole solution; the motion of each atom is characterised by an energy and a momentum related by an expression of the form (2). It is shown that unless the impurities move with about the speed of sound they will not produce any new excitations in the superfluid. Hence they collide only with phonons and rotons and move with the normal fluid. This is of course in agreement with observations previously made on superfluid flow by DAUNT, PROBST, JOHNSON, ALDRICH and NIER [82].

The above approach was developed by POMERANČUK [83] to predict the velocity of second sound in ^{3}He - ^{4}He solutions. He supposes that there are excitations associated with each impurity atom, specified by either equation (2) or equation (3) with the parameter μ replaced by μ', the « effective mass » of the particular impurity. By repeating Landau's original calculation but taking into account these extra excitations POMERANČUK obtains expressions for ϱ_n and the entropy of the solutions. The presence of the impurities leads to a new term in the thermodynamic potential which is used in the Landau equation for the acceleration of the superfluid. By solving the equations of motion again, values are obtained for the velocity of second sound when impurities are present. Roughly speaking, at comparatively high temperatures the effect of the impurities is to increase the entropy and hence increase the velocity, while at lower temperatures the impurities tend principally to increase ϱ_n and the velocity falls below the value for pure ^{4}He. At the lowest temperatures (~ 0.1 °K) the degeneracy of the statistics becomes important and the position is more complicated; POMERANČUK predicts that the velocity will tend to a constant value much smaller than $c/\sqrt{3}$.

The first experimental observations by LYNTON and FAIRBANK [84] were in general agreement with the previously predicted rise in velocity; as the lowest temperature reached was only 1.2 °K the fall in velocity at lower temperatures was not observed. These results were examined by HALATNIKOV [85] who showed that good agreement is obtained using an energy spectrum of type (2) with $\mu' = 8.5m$, where m is the mass of the proton. For an impurity spectrum of type (3) however no one value of μ' could be found to represent all the results and therefore HALATNIKOV concluded that this spectrum is probably not valid for ^{3}He atoms. He also used Pomerančuk's

formula to calculate the velocity of sound as a function of temperature and concentration: a very pronounced maximum in the curves is predicted at about 1.0 °K. Recent measurements at two different concentrations by KING and FAIRBANK [86] down to 0.2 °K are in good accord with these predictions. These experiments also show the profound effect that small quantities of ^{3}He have on the properties of ^{4}He: at low temperature the addition of ^{3}He produces very large changes in the value of ϱ_n.

HALATNIKOV [87] has recently treated the equations of motion of ^{3}He-^{4}He solutions with greater generality. He deduces [88] that, on the addition of ^{3}He to ^{4}He, two more kinetic coefficients (of diffusion and of thermal diffusion) are necessary to describe the motion, and he then evaluates the absorption coefficients for first and second sound. He also gives an expression for the velocity of second sound which for weak mixtures reduces to that of POMERANČUK. As in all the Russian treatments of this subject, there is some obscurity in the basic postulates. For example it is not obvious why the spectrum of a ^{3}He *atom* is similar to that of an elementary *excitation* in ^{4}He. Then it is not really clear how the treatment is affected by the presence or absence of superfluidity in pure ^{3}He; see [81] and [87]. HALATNIKOV [35] has also treated the propagation of shock waves of second sound in ^{3}He-^{4}He solutions.

11. – The Properties of Pure ^{3}He.

11·1. – ^{3}He *and* ^{4}He.

Although experimental data is still rather sparse, it appears that liquid ^{3}He does not exhibit either a specific heat anomaly or superfluidity above about 1 °K, and DAUNT and HEER [89] have deduced that if a mobile film of ^{3}He exists at all it only does so at temperatures lower than 0.25 °K. LANDAU in his treatment of helium II does not discuss what behaviour is to be expected of pure liquid ^{3}He, but there is no obvious reason why his theory should not apply to it. Actually, in order to ensure superfluidity, LANDAU has to assume that in ^{4}He the lowest roton level is above rather than below the lowest phonon level; in ^{3}He the position might conceivably be different. Also as LANDAU does not give a satisfactory picture of the mechanism responsible for the critical velocities it may be that a more complete treatment of this problem would indicate a difference between the two isotopes. Certainly however, LANDAU did not suggest that ^{3}He would be significantly different from ^{4}He.

There is no Russian discussion of this weakness in Landau's theory, and almost the only approach to the problem of why ^{3}He and ^{4}He behave differently is due to F. LONDON [90] who suggested that the λ transition in liquid ^{4}He corresponds to the order-disorder transition in a degenerate B. E. gas.

This is in many ways an attractive suggestion. ^{4}He should obey B.E. statistics, and the temperature at which the ordering begins in a B.E. gas of the same density as liquid helium is quite similar to that of the λ-point. The normal and super « fluids » may be identified with the excited and ground states, and since ^{3}He should obey F.D. statistics its behaviour should be substantially different from that of ^{4}He. So far however no one has succeeded in deducing the properties of liquid helium from those of a B.E. gas, almost certainly because even liquid helium with its large molar volume cannot be regarded as a gas. LANDAU in particular has criticised this model as he maintains that the atoms in the ground state must collide with excited atoms and superfluidity would be impossible. Evidence against the B. E. model also comes from a study of the scattering of light by liquid helium. GALANIN [91] and SCHIFF [92] have shown that a B.E. gas model should give rise to comparatively intense scattering near the λ-point, whereas GINZBURG [93] following LANDAU deduces that the scattering should be very small; experiments by JAKOVLEV [94] show only very little scattering and this does not vary on passing the λ-point. The position as to the scattering of thermal neutrons is rather similar. AHIESER and POMERANČUK [95] following LANDAU have shown that very little scattering is to be expected whereas a B.E. model leads to much more. Measurements of transmission coefficients [96] and recent experiments on the forward scattering of cold neutrons [97] show that the effects are less than predicted by the B.E. model. This point has recently been confirmed by X-ray investigations [98].

In spite of these objections to the B.E. model, BOGOLJUBOV [99] claims to show that a B.E. gas of mutually repellent particles may be described in terms of elementary excitations which are characteristic of the whole gas and cannot be identified with individual atoms. The energy spectra of these excitations are similar to those deduced by LANDAU and hence give some support to them. However this work hardly provides support for Landau's hydrodynamics as is sometimes suggested by the Russians, for these hydrodynamics are deduced entirely without reference to B.E. statistics. Although the position is obscure, it seems likely that the statistics do play a part in differentiating between ^{3}He and ^{4}He. In this connection a remark by TEMPERLEY [100] is worthy of notice: whereas the normal density ϱ_n of a B.E. gas calculated by Landau's method turns out to be less than ϱ, ϱ_n for a Fermi gas (like that of an ideal Boltzmann gas) turns out to be equal to ϱ.

11·2. – ^{3}He.

The only Russian approach to ^{3}He has been to ignore LANDAU's work and begin again from a model of ^{3}He as a degenerate Fermi gas of particles with spin 1/2. POMERANČUK [101] has thus obtained expressions for the coefficients

of viscosity and thermal conductivity which agree with the calculations of other workers. Very preliminary measurements on the viscosity had previously been reported [102]; these suggest that the viscosity rises with falling temperature as do the theoretical values. The most interesting implication in Pomerančuk's treatment is that if a degenerate Fermi gas is a sufficiently good model of liquid ^{3}He, then exchange effects will lead to an antiparallel orientation of the nuclear spins. As the magnitude of this energy is stated (but not proved) to be of the same order as the total energy of interaction, ordering of the nuclei should set in at temperatures of the *order* of 1 °K. (See also GOLDSTEIN and GOLDSTEIN [103]). Moreover, as the wave functions of the ^{3}He atoms must be much more localised in the solid state, the exchange interaction will be much smaller and alignment will only be brought about by magnetic interaction between the nuclei at about 10^{-7} °K. Hence at sufficiently low temperatures the entropy of the solid will be greater than that of the liquid and the melting pressure will rise with decreasing temperature.

At present there is little experimental data with which to judge these theories. No evidence is available on the magnetic properties of ^{3}He save that SYDORIAK and HAMMEL [104] have reported that the permeability is less than about 2. Recently however CHEN and LONDON [105] have announced that proton resonance measurements are in progress on both the liquid and solid; these should yield valuable information. In the absence of any specific heat data LIFŠIC [106] and others have attempted to deduce the entropy of the liquid from the observed vapour pressure curve. There is little agreement between these authors, principally because they make different assumptions about the behaviour of the entropy associated with the nuclear spins.

12 – Feynman's Theory.

While this paper has been in proof, FEYNMAN has published a theory of liquid helium which is very relevant to any discussion of LANDAU's work. In essence, FEYNMAN has derived the same picture of the liquid as Landau, but he has given it a more satisfactory physical foundation than Landau's quantum hydrodynamics. Moreover several points in the Russian work, hitherto obscure, are now more comprehensible. Without going into any detail, we now refer briefly to those points in his theory which are relevant to our previous remarks.

FEYNMAN regards the liquid as consisting of helium atoms which have the usual attractive and repulsive forces, and obey B.E. statistics. Because of the large atomic volume it is also postulated that the atoms may move very freely among one another. By considering the partition function for this model FEYNMAN [107] deduces that the strong attractive forces will not appre-

ciably affect the original picture given by F. LONDON [108] who compared the transition in the liquid with a condensation in a B.E. gas. Of course, if we accept this treatment the absence of a similar transition in ^{3}He is fully accounted for.

In a second paper [109], FEYNMAN considers the nature of the thermal excitations in helium. He argues, on general grounds, that the excitations of lowest energy will be compressional waves or phonons, and demonstrates by means of his new formulation of the partition function that such waves are possible in his model. Then qualitative reasoning in which the B.E. statistics play an essential role leads to the conclusion that there must be an energy gap between the ground state and the lowest of any other excitations. Finally in a third paper [110] FEYNMAN puts his argument in a more quantitative form and deduces a spectrum for the excitations in terms of the correlation function which is known from X-ray scattering. For small wave numbers this spectrum corresponds to the relation $\varepsilon = cp$, but for wave numbers of the order of the reciprocal of the atomic spacing, a minimum occurs corresponding to $\varepsilon = \Delta + (p - p_0)^2/2\mu$; this is of course similar to the spectrum which Landau postulated, apparently intuitively, in 1947. (See §§ **2**·1 and **6**·3). As FEYNMAN discusses in his second paper [109] these excitations will behave very much as Landau's phonons and rotons and will give rise to many of the phenomena characteristic of liquid helium. Also it seems [111] that the new theory can justify the treatment of ϱ_n as an invariant mass (see § **7**·3) and also the use of a roton type spectrum for atoms of ^{3}He in ^{4}He (see § **6**·4). However, the question of why the λ-point should be characterized by the relation $\varrho_n = \varrho$ remains obscure.

Finally, to sum up, we can say that LANDAU's theory, placed on a firmer basis by FEYNMAN, gives a good account of nearly all the properties of liquid helium II. It should be noted however that while there is a great bulk of experimental data for the temperature region above 0.8 °K in which the rotons predominate, the data below this temperature is still rather scarce. For example, consider the determination of the important parameter ϱ_n. At the higher temperatures this has been found quite independently from the velocity of second sound and the specific heat and from Andronikašvili's experiment; below 0.8 °K however the position on second sound still seems obscure (§ **7**·1) and Andronikašvili's experiment has not been attempted because of experimental difficulties. Data on the fountain pressure below 1 °K is also scanty (*), although its value is predicted unequivocally by both LANDAU and FEYNMAN. Thus it seems as if the full verification of Landau's theory still rests with the experimentalists.

(*) Actually a preliminary measurement by BOTS and GORTER [112] suggests that there may be some discrepancy with theory.

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14. – Bibliography.

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ABSTRACT

OF THE INTERNATIONAL SYSTEM

OF TRANSLITERATION OF CYRILLIC CHARACTERS

(2ND DRAFT ISO RECOMMENDATION N. 6)

ADVISED BY THE EDITORIAL BOARD

OF

IL NUOVO CIMENTO

Cyrillic Character		Transliteration from :					Examples & Remarks
		Bulg-arian	Russ-ian	Ukrai-nian	White Russ.	Serb-ian	
1.	А, а	a	a	a	a	a	Адрес = Adres
2.	Б, б	b	b	b	b	b	Ваба = Baba
3.	В, в	v	v	v	v	v	Вы = Vy
4.	Г, г	g	g	g	g	g	Глава = Glava Голова = Golova
5.	Ґ, ґ			ġ	ġ		ґреци = Ġreci
6.	Д, д	d	d	d	d	d	Да = Da
7.	Ђ, ђ					đ	Croat dj and gj changed to đ in alphabetized headings
8.	Е,е (ë)	e	e(ë)	e	e(ë)	e	Еще = Ešče
9.	Є, є			je			Твоє = Tvoje
10.	Ж, ж	ž	ž	ž	ž	ž	Журнал = Žurnal
11.	З, з	z	z	z	z	z	Звезда = Zvezda
12.	S, s						(not used)
13.	И, и	i	i	y	i		Или = Ili
14.	І, і		i	ı	i	ı	
15.	Ї, ї			ï			Їзда = Iżda
16.	J, j					j	
17.	Й, й	j	j	j	j	j	-ый,-ий,-ой =-yj,-ij,-oj
18.	К, к	k	k	k	k	k	Как = Kak
19.	Љ, л	l	l	ll	l	l	Любить = Ljubit'
20.	Љ, љ					lj	
21.	М, м	m	m	m	m	m	Муж - Muž
22.	Н, н	n	n	n	n	n	Нижний = Nižnij
23.	Њ, њ					nj	
24.	О, о	o	o	o	o	o	Общество = Obščestvo

(×) Cyrillic ë to be transliterated by ë only when diacritical appears in the original.

Cyrillic Character		Transliteration from :					Examples & Remarks
		Bulgarian	Russian	Ukrainian	White Russ	Serbian	
25.	П, п	p	p	p	p	p	Первый = Pervyj
26.	Р, р	r	r	r	r	r	Рыба = Ryba
27.	С, с	s	s	s	s	s	Сестра = Sestra
28.	Т, т	t	t	t	t	t	Товарищ = Tovarišč
29	Ћ ћ					ć	
30.	У, у	u	u	u	u	u	Утро = Utro
31.	Ф, ф	f	f	f	f	f	Физика = Fizika
32.[×]	Х, х	h	h	h	h	h	Химческий = Himičeskij
33.	Ц, ц	c	c	c	c	c	Центральный = Central'nyj
34.	Ч, ч	č	č	č	č	č	Часы = Časy
35	Џ, џ					dž	
36.	Ш, ш	š	š	š	š	š	Школа = Škola
37.	Щ, щ	št	šč	šč	šč		Щека = Ščeka
38	(medial) Ъ, ъ (final)	ă ŭ	"or" Not transliterated	"or"	"or"		In modern Russian, where ' replaces medial ъ, transliteration is still '".
39.	Ы, ы	y	y				Был = Byl
40.	Ь, ь	or'	'or'	'or'	'or'		Маленький = Malen'kij
41.	Ѣ, ѣ	ě	ė	ě	ě		Ѣсть = Ěst'
42.	Э, э		ė		ė		Это = Ėto
43.	Ю, ю	ju	ju	ju	ju		Южный = Južnyj
44.	Я, я	ja	ja	ja	ja		Яйцо = Jajco

([×]) Countries with a firmly established tradition in favour of ch or kh may use whichever of these two is the more appropriate, provided that, in catalogues, indexes etc. containing the variant, permanent cross-references are made to and from the h.

Added by Editorial Board of *Il Nuovo Cimento*

In the Reviews published in *Il Nuovo Cimento* x is transliterated in h. Place names commonly transcribed into another language (*e.g.* Moscow in English) can be retained in their traditional form.

INDICE DEL SUPPLEMENTO

AL VOLUME X, SERIE IX, DEL

NUOVO CIMENTO

Anno 1953

G. Bozza – La birifrangenza delle fibre artificiali (Parte I) . . . . . pag. 1

G. Bozza e E. Bonauguri – La birifrangenza delle fibre artificiali (Parte II) » 24

G. Bozza – Sul meccanismo dei processi di filatura dei tessili artificiali . . » 55

E. Corinaldesi – Some Aspects of the Problem of Measurability in Quantum Electrodynamics . . . . . » 83

O. E. H. Rydbeck – Some Wave Propagation Properties of the Electron Beam in Vacuum and in Ionized Media . . . . . » 101

G. Puppi – Bilancio energetico della radiazione cosmica . . . . . » 115

G. Latmiral – Rivestimenti assorbenti per microonde . . . . . » 147

Th. Vogel – Servomécanismes, cybernétique et information . . . . . » 166

Atti del XXXVIII Congresso tenutosi a Bergamo nei giorni 25-28 Settembre 1952 . . . . . » 197

Rassegne di lavori di Fisica pubblicati negli ultimi anni in Europa orientale e particolarmente in Russia . . . . . » 341

Abstract of the International System of Transliteration of Cyrillic Characters » 539

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